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TRANSLATION

PHYSICS OF SHOCK WAVES AND HIGH-TEMPERATURE HYDRODYNAMIC PHENOMENA

By

Ya. B. Zel'dovich and Yu. P. Rayzer

FOREIGN TECHNOLOGY DIVISION

AIR FORCE SYSTEMS COMMAND

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EDITED MACHINE TRANSLATION

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By: Ya. B. Zel'dovich and Yu. P. Rayzer

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Ya. B. Zel'dovich i Yu. P. Rayzer

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Moskva 1963

Pages 1-632

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U. S. BOARD ON GEOGRAPHIC NAMES TRANSLITERATION SYSTEM

Block	Italic	Transliteration	Block	Italic	Transliteration
А а	*А а*	A, a	Р р	*Р р*	R, r
Б б	*Б б*	B, b	С с	*С с*	S, s
В в	*В в*	V, v	Т т	*Т т*	T, t
Г г	*Г г*	G, g	У у	*У у*	U, u
Д д	*Д д*	D, d	Ф ф	*Ф ф*	F, f
Е е	*Е е*	Ye, ye; E, e*	Х х	*Х х*	Kh, kh
Ж ж	*Ж ж*	Zh, zh	Ц ц	*Ц ц*	Ts, ts
З з	*З з*	Z, z	Ч ч	*Ч ч*	Ch, ch
И и	*И и*	I, i	Ш ш	*Ш ш*	Sh, sh
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К к	*К к*	K, k	Ъ ъ	*Ъ ъ*	"
Л л	*Л л*	L, l	Ы ы	*Ы ы*	Y, y
М м	*М м*	M, m	Ь ь	*Ь ь*	'
Н н	*Н н*	N, n	Э э	*Э э*	E, e
О о	*О о*	O, o	Ю ю	*Ю ю*	Yu, yu
П п	*П п*	P, p	Я я	*Я я*	Ya, ya

* ye initially, after vowels, and after ъ, ь; e elsewhere. When written as ё in Russian, transliterate as yë or ë. The use of diacritical marks is preferred, but such marks may be omitted when expediency dictates.

FOLLOWING ARE THE CORRESPONDING RUSSIAN AND ENGLISH DESIGNATIONS OF THE TRIGONOMETRIC FUNCTIONS

Russian	English
sin	sin
cos	cos
tg	tan
ctg	cot
sec	sec
cosec	csc
sh	sinh
ch	cosh
th	tanh
cth	coth
sch	sech
csch	csch
arc sin	$\sin^{-1}$
arc cos	$\cos^{-1}$
arc tg	$\tan^{-1}$
arc ctg	$\cot^{-1}$
arc sec	$\sec^{-1}$
arc cosec	$\csc^{-1}$
arc sh	$\sinh^{-1}$
arc ch	$\cosh^{-1}$
arc th	$\tanh^{-1}$
arc cth	$\coth^{-1}$
arc sch	sech^{-1}
arc csch	csch^{-1}

rot	curl
lg	log

DEFINITIONS OF CYRILLIC ITEMS

авт = self
адиаб = adiab

бар = bar

в = hv
ВВ = VV
внутр = int
В.О. = V.O.
вр = rot
в.р. = RW (r.w.)
вращ = rot

Г = G
газ = gas
гидрод = hydrod
граница = bound

дис = dis
дис.рек. = dis.rec.
дно = bot
д.р. = d.r.

зах, захв = cap
зв = sou

ж = liq

ид = id
изл = rad
ион(из) = ion(iz)

К = C
к, кол = vib
кв = kv
квант = quant
кин = kin
класс = class
кр = crit
кул = coul

М = T
молек = molec

нач = init
неид = nonid
норм = nor
Н.П. = N.P.

обм, обмен = exch
ост = res
отв = open
О.Ш. = O.Sh.

п = p
П = P
пар = vap
ПВ = PV
пг = pg
полн = tot, full
порист = por
пост = trans
пост.одн = one-dim.trans.
пот = pot
пр = lim
прям = str

р = p
расч = cal
рек = rec
рел, релак = rel

сег = segm
сек = sec
сплош = sol
ср = av
ст = stat
ст = col

Cyrillic items continued

т = t
теп = therm
тор = brak
торм = decel
Т.Ф. = T.F.
Т.Ф.Д. = T.F.D.

у = s
у.в. = s.w.

ф = f
Ф.А. = F.A.
Ф.У.В. = F.U.V.

ш = sh
Ш-Р = Sch-R

эв = ev
эл = el
эрг/г = erg/g
эф = ef

ANNOTATION

This book constitutes the first attempt in the world literature to systematically consider the extensive range of questions from different regions of physics, physical chemistry and astrophysics with which contemporary gas- and hydrodynamics deals. In it there are expounded fundamentals of gas dynamics and theory of shock waves, transport theory of radiation. There are studied thermodynamic and optical properties of substances at high temperatures and pressures, kinetics of dissociation, ionization and other non-equilibrium processes, phenomena connected with radiation of light and radiant heat transfer in shock waves and during explosions, problems of propagation of shock waves in solid bodies, etc. To the authors of the monograph there belong a large number of original works in the considered region of science, which have been reflected in this book.

The book will serve as a valuable practical aid for wide groups of physicists, mechanicians and engineers studying applied physics and new technology. It will be useful to students and post graduates in the corresponding specialties, and also to all physicists and mechanicians wishing to become acquainted with contemporary state of science of shock waves.

PREFACE

Problems of contemporary technology have demanded from science penetration into the region of "high parameters" of state of a substance: high concentrations of energy, high temperatures and pressures, high velocities. In practice such conditions are realized in strong shock waves, during explosions, during very fast supersonic motions of bodies in the atmosphere, in powerful electrical discharges, etc.

At high temperatures in gasses there occur various physical and physicochemical processes: excitation of molecular vibrations, dissociation, chemical reactions, ionization, radiation of light. These processes affect thermodynamic properties of gases, and during sufficiently fast motions and sufficiently fast changes of state of a substance, motion is influenced by kinetics of these processes. An especially important role at very high temperatures is played by processes connected with emission and absorption of radiation and radiant heat transfer. Above-mentioned processes frequently present interest not only from the point of view of their energy influence on motion of gas: they cause change of composition of gas, of its electrical properties, lead to luminescence of gas and appearance of many optical effects, etc. A considerable part of this book is dedicated to the study of all these problems—to all that composes the content of the newly appearing branch of science, "physical gas dynamics."

Great scientific and practical interest is presented by study of strong shock waves in solid bodies. Recent achievements which have made it possible with the help of shock waves to compress solid bodies up to millions of atmospheres have opened new ways of investigation of state of solid matter at super-high pressures. To these questions there also is given considerable attention in this book.

In the described area there are closely interconnected many branches of science: gas dynamics, theory of shock waves, thermodynamics and statistical physics, molecular physics, physical and chemical kinetics, physical chemistry, spectroscopy, theory of radiation, elements of astrophysics, solid state physics, and others. Many of the physical phenomena and processes considered here have different character and in no way are connected with each other. A result of such heterogeneity of the material was the absence of continuity in contents of the book. Certain chapters have an independent character, pertain to absolutely different regions of physics or mechanics, and not all chapters are related to each other. Therefore, for the reader interested only in one or more particular topics, it is sufficient to become acquainted only with the corresponding chapters.

In examining the most diverse questions, even those of a mathematical character, we tried first of all to explain physical essence of phenomena with the help of simple mathematical means, while widely using estimates and semiqualitative analysis. At the same time, we tried to help those physicists, mechanicians, and engineers who work in the corresponding regions of applied physics and technology, and to give to them practical means for independent analysis of complicated and diverse physical phenomena.

With this goal, consideration of majority of phenomena is carried through to numerical results; formulas for calculation and estimates of different quantities are written in form which is convenient for practical work; there are presented many useful experimental data and information of reference type, etc.

This book has a theoretical character, and description of experimental installations and methods is reduced to a minimum. However, the account of results of experiment and comparison of them with results of theoretical calculations and estimates has been given proper attention.

Periodic literature on "physical gas dynamics" is huge. However, as far as we know, neither in Soviet nor in foreign literature have there yet been made attempts to systematize, generalize, and expound from a single point of view in one book the material pertaining to this new region of science. Apparently, this book constitutes the first attempt in this direction.

The book was written during 1960-1961, which determines the basic level of the literature used. However, in sections concerning areas whose ideas are being developed at an especially fast rate, there later have been introduced short supplements and references to the latest literature. This pertains basically to Chapters V, VI, VII.

Variety of phenomena and extensiveness of material forced us to be limited to consideration of not nearly all questions which have a relation to the studied region. We do not consider the mathematical side of hydrodynamics, of such a problem as supersonic flow around bodies; we almost do not touch upon electromagnetic phenomena; absolutely do not concern ourselves with questions of thermonuclear fusion, behavior of plasma in magnetic field, all that pertains to magnetohydrodynamics and magnetogasdynamics, problems of combustion and detonation and so forth. On all these topics there already are a great number of books.

Selection of material of this book to a certain extent is subjective. An important place is allotted to consideration of phenomena which the authors investigated in their own works. Thus, on original works are almost completely based Chapters VIII and IX; to a great extent also VII, X, XII, and partially Chapter XI. Chapter I constitutes the result of basic revision of an early book of one of the authors: "Theory of Shock Waves and Introduction to Gas Dynamics", which was published in 1946 in Publishing House of Academy of Sciences of USSR.

We would like to express special thanks to A. S. Kompaneyets, who is responsible for development of a number of questions discussed in this book, for many useful discussions and remarks made during reading of the manuscript. We are thankful to L. B. Al'tshuler and S. B. Kormer, on whose works to a considerable degree is based Chapter XI of the book, for remarks made during reading of the manuscript of this chapter. We are thankful also to M. A. Yel'yashevich, who attentively read the manuscript and made valuable remarks.

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Pages: Cover-632.

CHAPTER I

ELEMENTS OF GAS DYNAMICS AND CLASSICAL THEORY OF SHOCK WAVES

1. Continuous Flow of an Inviscid and Non-Thermally-Conducting Gas

§ 1. Equations of Gas Dynamics

For high compression of liquids (and solid bodies) there are needed pressures of hundreds of thousands of atmospheres and above. Therefore, under usual conditions a liquid can be considered as an incompressible medium. Velocities of flow of liquid during small changes of density are much less than speed of sound, which is the scale of velocity characterizing a continious medium. During small changes of density and motions which are slow as compared to speed of sound, gas also can be considered to be incompressible, and its motion can be described with the help of hydrodynamics of an incompressible fluid. However, large changes of density and velocity of flow comparable with speed of sound in gasses, in distinction from liquids, are attained comparatively easily: at pressure drops of order of magnitude of the actual pressure, i.e., at $\Delta p \sim 1$ atm, if initial pressure of gas is atmospheric. Under such conditions it is necessary to consider compressibility of the substance. Equations of gas dynamics thus differ from equations of hydrodynamics of an incompressible fluid in that in them there is considered possibility of large changes of density of the substance.

State of moving gas with known thermodynamic properties is determined by specifying speed, density, and pressure as functions of coordinates and time. For finding these functions there serves the system of equations of gas dynamics, which is composed, in differential form, of the general laws of conservation of mass, momentum and energy of a substance.

Let us write these equations without derivation, which can be found, for instance, in book of L. D. Landau and Ye. M. Lifshits [1]. We will disregard action of body forces (gravity), and also viscosity and thermal conduction of substance.* Let us designate by $\partial/\partial t$ partial derivative with respect to time referred to a given point of space, the local derivative, and by d/dt the particle derivative, which characterizes change in time of some quantity, connected with a given moving particle of substance. If u is velocity vector of particle with components u_x, u_y, u_z or u_i, where $i = 1, 2, 3$, then

$$\frac{d}{dt}=\frac{\partial}{\partial t}+(u\nabla). \tag{1.1}$$

First equation is continuity equation; it indicates conservation of mass of the substance, i.e., to the fact that change of density ρ in given element of volume occurs due to inflow (or outflow) of substance into this element:

$$\frac{\partial\rho}{\partial t}+\operatorname{div}\rho u=0. \tag{1.2}$$

---

*Equations of gas dynamics taking into account viscosity and thermal conduction will be considered below, in § 20.

With help of definition (1.1), continuity equation can be written in the form

$$\frac{d\rho}{dt}+\rho\operatorname{div}\boldsymbol{u}=0. \qquad (1.3)$$

In the particular case of an incompressible liquid, when ρ = const, continuity equation is simplified:

$$\operatorname{div}\boldsymbol{u}=0. \qquad (1.4)$$

Second equation expresses Newton's law and does not differ from equation of motion of an incompressible liquid (p is pressure):

$$\rho\frac{d\boldsymbol{u}}{dt}=-\nabla p \qquad (1.5)$$

or, in the form of Euler's equation,

$$\frac{\partial\boldsymbol{u}}{\partial t}+(\boldsymbol{u}\nabla)\boldsymbol{u}=-\frac{1}{\rho}\nabla p. \qquad (1.6)$$

As it is easy to verify by means of direct calculation, equation of motion together with continuity equation is equivalent to law of conservation of momentum, written in a form analogous to equation (1.2),

$$\frac{\partial}{\partial t}\rho u_i=-\frac{\partial\Pi_{ik}}{\partial x_k}, \qquad (1.7)$$

where Π_{ik} is tensor of momentum flux density

$$\Pi_{ik}=\rho u_i u_k+p\delta_{ik}. \qquad (1.8)$$

Equation (1.7) expresses the fact that change of i-th component of momentum at given point of space is connected with outflow (inflow) of momentum together with mass (first term in (1.8)) and work of forces of pressure (second term).*

Third equation is essentially new as compared to hydrodynamics of an incompressible liquid and is equivalent to first law of

---

*In the right side of formula (1.7) there is produced summation over the twice met index k(k = 1, 2, 3); δ_{ik} = 1 when i = k and δ_{ik} = = 0 when i ≠ k.

thermodynamics — the law of conservation of energy. It is possible to read it thus: change of specific internal energy ε of a given particle of substance occurs due to work of compression, which is produced on it by its surrounding medium, and also due to energy release from outside sources:

$$\frac{d\varepsilon}{dt}+p\frac{dV}{dt}=Q. \qquad (1.9)$$

Here V = 1/ρ is specific volume, and Q is energy release per second per gram of substance from external sources (Q can also be negative if there are nonmechanical losses of energy, for instance due to radiation).

With help of continuity equation and equation of motion, the energy equation also can be reduced to a form similar to (1.2), (1.7):

$$\frac{\partial}{\partial t}\left(\rho\varepsilon+\frac{\rho u^2}{2}\right)=-\operatorname{div}\left[\rho u\left(\varepsilon+\frac{u^2}{2}\right)+pu\right]+\rho Q. \qquad (1.10)$$

Physical meaning of this equation is that change of total energy of unit of volume at given point of space occurs due to outflow (inflow) of energy during motion of the substance, work of forces of pressure and energy release from external sources.

Equations continuity, motion and energy form a system of the five equations (equation of motion is a vector equation and equivalent to three coordinate equations) in five unknown functions of coordinates and time: ρ, u_x, u_y, u_z, p. External sources of energy Q are considered to be given, and internal energy ε can be expressed in terms of density and pressure, inasmuch as thermodynamic properties of substance are assumed to be known: $\varepsilon = \varepsilon\ (p, \rho)$.

If energy, as this frequently happens, is known not as a function of pressure and density, but as a function of temperature T and density or temperature and pressure, then to this system we should add the equation of state of substance $p = f\ (T,\ \rho)$. Equation of state of ideal gas has the form

$$pV = AT,\quad p = A\varrho T, \tag{1.11}$$

where A is gas constant calculated for 1 gram.*

Energy equation (1.9) has general significance and is valid even when substance is not in thermodynamic equilibrium. In that particular case, which is most important in practice, when substance is in thermodynamic equilibrium, it is possible to write it in different form with help of the second law of thermodynamics

$$T\,dS = d\varepsilon + p\,dV, \tag{1.12}$$

where S is specific entropy. In absence of external sources of heat, third equation of gas dynamics is equivalent to equation of constancy of entropy of a particle, i.e., to condition of adiabaticity of motion

$$\frac{dS}{dt} = 0. \tag{1.13}$$

In an ideal gas with constant heat capacity, entropy is especially simply expressed in terms of pressure and density (specific volume)

$$S = c_V \ln pV^\gamma + \text{const}, \tag{1.14}$$

where γ is adiabatic index, equal to specific heat ratio at constant pressure and constant volume $\gamma = c_p/c_V = 1 + A/c_V$. In this case adiabatic equation (1.13) (or energy equation) can be directly written in form of differential equation relating pressure and density (pressure and volume),

$$\frac{1}{p}\frac{dp}{dt} + \gamma\frac{1}{V}\frac{dV}{dt} = 0. \tag{1.15}$$

To this system of differential equations of gas dynamics there are added corresponding initial and boundary conditions.

---

*$A = R/\mu$, where R is universal gas constant, and μ is molecular weight.

§ 2. Lagrange Coordinates

Equations in which gas-dynamic quantities are considered as functions of spatial coordinates and time are called equations in Euler form or equations in Euler coordinates.

In the case of one-dimensional motions, i.e., plane, cylindrical and spherically symmetric, we frequently use other, Lagrange coordinates. In distinction from an Euler coordinate, a Lagrange coordinate is connected not with a fixed point of space, but with a definite particle of substance. Gas-dynamic quantities expressed as functions of Lagrange coordinates characterize changes of density, pressure and velocity of every particle of substance with flow of time. Lagrange coordinates are especially convenient in examining internal processes occurring in a substance which do not go beyond the bounds of a given particle: let us say a chemical reaction, the flow of which with passage of time depends on change of temperature and density of the particle. Introduction of Lagrange coordinates in a number of cases permits us to more briefly and easily find exact solutions of equations of gas dynamics, or makes numerical integration of the latter more convenient.

Time derivative in Lagrange coordinates is equivalent simply to particle derivative d/dt. Particle can be characterized by mass of substance, which distinguishes it from some other fixed particle, or by its coordinate at initial moment of time.

Introduction of Lagrange coordinates is especially simple in the plane case, when motion depends only on one Cartesian coordinate x. Let us designate current Euler coordinate of considered particle by x, and coordinate of some fixed particle by x_1 (as the fixed particle there may be, for instance, selected a particle near a solid wall or near boundary between gas and vacuum, if such exist in the problem). Then the mass of a column of unit cross section between considered particle and fixed particle is equal to

$$m=\int_{x_1}^{x} \rho\, dx, \tag{1.16}$$

and increment of mass upon transition from the particle to a neighboring one is

$$dm=\rho\, dx. \tag{1.17}$$

Quantity m can be selected as a Lagrange coordinate.

If at initial moment, as this frequently happens, gas is at rest, and its density is constant, $\rho(x, 0) = \rho_0$, then as Lagrange coordinate it is convenient to take initial coordinate of particle measured from point x_1; we will designate it by a. Then

$$a=\int_{x_1}^{x} \frac{\rho}{\rho_0}\, dx, \quad da=\frac{\rho}{\rho_0}\, dx. \tag{1.18}$$

Equations of plane motion of gas in Lagrange coordinates acquire simple form. Equation of continuity, written with respect to specific volume $V = 1/\rho$ and unique x-th component of velocity u is

$$\frac{\partial V}{\partial t}=\frac{\partial u}{\partial m} \quad \text{or} \quad \frac{1}{V_0}\frac{\partial V}{\partial t}=\frac{\partial u}{\partial a}. \tag{1.19}$$

Here, as and in subsequent equations, time derivative is particle derivative d/dt, but it is better to write it in the form of partial derivative $\partial/\partial t$, in order to stress that it is taken at m and a = = const, i.e., for a given particle with definite Lagrange coordinate m or a. Equation of motion in Lagrange coordinates has the form

$$\frac{\partial u}{\partial t}=-\frac{\partial p}{\partial m} \quad \text{or} \quad \frac{\partial u}{\partial t}=-V_0\frac{\partial p}{\partial a}. \tag{1.20}$$

Regarding, however, equation of energy written in form (1.9) or in form of condition of adiabaticity (1.13) (in the absence of external sources of heat and dissipative processes — viscosity and thermal conduction), they retain their form; it is necessary only to replace designation d/dt by $\partial/\partial t$. In an ideal gas with constant heat capacity, condition of adiabaticity (1.13) gives

$$pV^{\gamma}=f[S(m)], \tag{1.21}$$

where function f depends only on entropy of given particle m. In so-called isentropic motion, when entropies of all particles are identical and do not change in time, f = const, where equation $pV^{\gamma} = \text{const}$ is valid in Lagrange as well as in Euler coordinates.

It is essential that in the plane case, Euler coordinate x in explicit form is not contained in equation. After Lagrange equations are solved and there is found function V(m, t), it is possible to go over to dependence of gas-dynamic quantities on Euler coordinate with help of quadrature, by integrating equation (1.17),

$$dx=V(m,\,t)\,dm,\quad x(m,\,t)=\int_0^m V(m,t)\,dm+x_1(t). \tag{1.22}$$

In cylindrical and spherical cases, equations of gas dynamics in Lagrange coordinates are somewhat more complicated than in the plane case, since now in the equations there is contained in explicit form the Euler coordinate, and in the system of equations there is included an additional equation relating Lagrange and Euler coordinates. For instance, in spherical case, Lagrange coordinate can be defined as mass included inside spherical volume near center of symmetry:

$$m=\int_0^r 4\pi r^2\rho\,dr,\quad dm=4\pi r^2\rho\,dr. \tag{1.23}$$

If at initial moment, density of gas is constant, it is possible to take as Lagrange coordinate initial radius r_0 of the "particle." considered as an elementary spherical shell:

$$\frac{4\pi r_0^3}{3}\rho_0=\int_0^r 4\pi r^2\rho\,dr,\quad dr_0=\frac{r^2}{r_0^2}\frac{\rho}{\rho_0}\,dr. \tag{1.24}$$

Equation of continuity in spherical Lagrange coordinates is

$$\frac{\partial V}{\partial t}=\frac{\partial}{\partial m}4\pi r^2u \quad \text{or} \quad \frac{1}{V_0}\frac{\partial V}{\partial t}=\frac{1}{r_0^2}\frac{\partial}{\partial r_0}r^2u. \tag{1.25}$$

Equation of motion

$$\frac{\partial u}{\partial t}=-4\pi r^2\frac{\partial p}{\partial m} \quad \text{or} \quad \frac{\partial u}{\partial t}=-\frac{1}{\varrho_0}\frac{r^2}{r_0^2}\frac{\partial p}{\partial r_0}. \tag{1.26}$$

Energy equation or adiabatic equation remain the same as in the plane case.

As an additional equation, in the system there is included differential (or integral) relationship (1.23) or (1.24), which relates m and r or r_0 and r.

Equations for cylindrical case are formed fully analogously to the spherical case.

It is necessary to note that in two-dimensional and three-dimensional flows, transition to Lagrange coordinates, as a rule, is not advantageous, since equations are then greatly complicated.

§ 3. Sound Waves

Speed of sound is included in equations of gas dynamics as the speed of propagation of small perturbations. In the limiting case, when change of density and pressure $\Delta\rho$ and Δp during motion of substance are very small as compared to mean values of density and pressure ρ_0 and p_0, and velocities are small as compared to speed of sound c, equations of gas dynamics are transformed into equations of acoustics and describe propagation of sound waves.

Let us write density and pressure in the form $\rho = \rho_0 + \Delta\rho$, $p = p_0 + \Delta p$ and consider quantities $\Delta\rho$, Δp, and also velocity u as small quantities. Disregarding quantities of second order of smallness, we will transform Euler equations of continuity and motion for the plane case. Equation of continuity gives

$$\frac{\partial \Delta\rho}{\partial t} = -\rho_0 \frac{\partial u}{\partial x}. \tag{1.27}$$

Equation of motion acquires the form

$$\rho_0 \frac{\partial u}{\partial t} = -\frac{\partial p}{\partial x} = -\left(\frac{\partial p}{\partial \rho}\right)_S \frac{\partial \Delta\rho}{\partial x}. \tag{1.28}$$

In the last transformation it is taken into account that motion in sound wave is adiabatic. Therefore, small change of pressure is associated with small change of density through the adiabatic derivative: $\Delta p = (\partial p/\partial \rho)_S \Delta\rho$. This derivative constitutes, as we will now see, the square of the speed of sound

$$c^2 = \left(\frac{\partial p}{\partial \rho}\right)_S \tag{1.29}$$

and corresponds to unperturbed state of substance.

Differentiating the first of the written equations with respect to time, and the second with respect to coordinate, we will eliminate mixed derivative $\partial^2 u/\partial t\, \partial x$. Let us obtain wave equation for change of density

$$\frac{\partial^2 \Delta\rho}{\partial t^2} = c^2 \frac{\partial^2 \Delta\rho}{\partial x^2}. \tag{1.30}$$

The same equation is satisfied by the magnitude of change of pressure $\Delta\rho$, which is proportional to $\Delta p = c^2 \Delta\rho$, and also by velocity u and all other parameters of the substance, for instance, temperature.*
Wave equation of type (1.30) admits two groups of solutions:

$$\Delta\rho = \Delta\rho(x-ct), \quad \Delta p = \Delta p(x-ct), \quad u = u(x-ct) \tag{1.31}$$

and

$$\Delta\rho = \Delta\rho(x+ct), \quad \Delta p = \Delta p(x+ct), \quad u = u(x+ct) \tag{1.32}$$

(by c we mean the positive root $c = +\sqrt{(\partial p/\partial \rho)_S}$.

---

*In order to obtain wave equation for velocity, we will differentiate equation (1.30) with respect to time and use equations (1.27), (1.28):

$$\frac{\partial^3 \Delta\rho}{\partial t^3} = c^2 \frac{\partial^3 \Delta\rho}{\partial x^2 \partial t} = -\rho_0 \frac{\partial}{\partial x} \frac{\partial^2 u}{\partial t^2} = -c^2 \rho_0 \frac{\partial}{\partial x} \frac{\partial^2 u}{\partial x^2},$$

whence $\partial^2 u/\partial t^2 = c^2 \partial^2 u/\partial x^2 + f(t)$. Noticing that before the wave in unperturbed substance $u = 0$, we will find that $f(t) = 0$.

First group describes perturbation propagating in the direction of positive x axis, and the second describes perturbation propagating in the opposite direction. In the first case, for instance, given value of density corresponds to a definite value of the argument x - ct, i.e., with flow of time it goes in the direction of positive x with velocity c. Thus, c is velocity of propagation of sound waves.

Noticing that $\partial u(x \mp ct)/\partial x = \mp (1/c)\partial u(x \mp ct)/\partial t$, and taking into account the fact that in undisturbed gas before the wave u = 0, $\Delta\rho = 0$ (see footnote), we will find with help of equation (1.27) the relation between mass velocity of gas u and changes of density or pressure:

$$u = \pm \frac{c}{\varrho_0} \Delta\varrho = \pm \frac{\Delta p}{\varrho_0 c}, \quad \Delta\varrho = c^2 \Delta\varrho = \pm \varrho_0 c u. \tag{1.33}$$

Upper sign pertains to wave travelling in the direction of positive x, and the lower pertains to wave travelling in the direction of negative x.

In both cases mass velocity is in the direction of propagation of the wave where the substance is compressed, and in the opposite direction, where it is rarefied.

General solution of wave equations for $\Delta\rho$ and u is composed of two particular solutions, which correspond to waves travelling in positive and negative directions of the x axis. According to (1.31), (1.32), (1.33), solutions for density and velocity can be written in the following form:

$$\Delta\varrho = \frac{\varrho_0}{c} f_1(x - ct) + \frac{\varrho_0}{c} f_2(x + ct), \tag{1.34}$$

$$u = f_1(x - ct) - f_2(x + ct), \tag{1.35}$$

where f_1 and f_2 are arbitrary functions of their arguments which are determined by initial distributions of density and velocity:

$$f_1 = \frac{1}{2}\left[\frac{c}{\varrho_0} \Delta\varrho(x, 0) + u(x, 0)\right],$$

$$f_2 = \frac{1}{2}\left[\frac{c}{\varrho_0} \Delta\varrho(x, 0) - u(x, 0)\right].$$

For instance, if at initial moment there is a rectangular perturbation of density, and gas everywhere is motionless, then to the right and to the left there begin to travel rectangular perturbations, as shown in Fig. 1.1.

If at initial moment, distributions of density and velocity have the form depicted in Fig. 1.2, where $u = \frac{c}{\rho_0} \Delta\rho$, so that $f_2 = 0$, then rectangular pulses will travel only in one direction. (Such a perturbation can be created by a piston which at initial moment starts to be thrust into gas at rest with constant velocity u, and after a certain time is "instantaneously" stopped. If length of rectangular pulse is equal to L, then, obviously, time of action of piston $t_1 = L/c$).

Special importance for acoustics is presented by monochromatic sound waves, in which all quantities are periodic functions of time of the type

$$f = A\cos\left(\frac{\omega}{c}x - \omega t\right),$$

or, in complex form,

$$f = A\exp\left[-i\omega\left(t - \frac{x}{c}\right)\right].$$

$\nu = \omega/2\pi$ is frequency of sound, and $\lambda = c/\nu$ is wave length. Any perturbation can be expanded in a Fourier integral, i.e., can be represented in the form of a set of monochromatic waves with different frequencies.

Sounds perceived by human ear have frequency ν from 20 to 20,000 cps (oscillations per second) and wave lengths corresponding to speed of sound in atmospheric air c = 330 m/sec,* from 15 m to 1.5 cm.

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*Adiabatic index of air under normal conditions

$$\gamma = 1.4, \quad c = (\partial p/\partial \rho)_S^{1/2} = (\gamma p_0/\rho_0)^{1/2} = (\gamma A T_0)^{1/2}$$

(since for S = const $p \sim \rho^{\gamma}$).

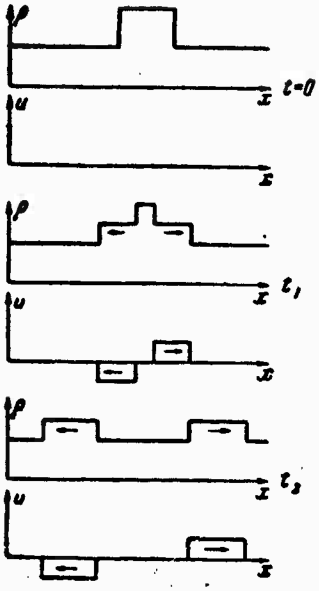

Fig. 1.1. Propagation of rectangular pulse of density and pressure along one coordinate in linear acoustics.

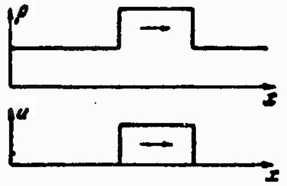

Fig. 1.2.

For an idea of the numerical values of different quantities in a sound wave, we will indicate that for the strongest sound, which is 10^5 times more intense* than the fortissimo of an orchestra, amplitude of change of air density in wave is 0.4% of normal density; amplitude of change of pressure is 0.56% of atmospheric; amplitude of velocity is 0.4% of velocity of sound, i.e., 1.3 m/sec. Amplitude of displacement of particles of air is of the order of $\Delta x \approx u/2\pi\nu = (u/c)\ (\lambda/2\pi) \approx \approx 6\cdot 10^{-4}\ \lambda$ ($\Delta x \approx 0.036$ cm for $\nu = 500$ cps).

Let us find energy connected with small a perturbation which is propagated through a gas at rest. Increase of specific internal energy of perturbed substance with accuracy up to terms of the second order of smallness with respect to $\Delta\rho$ (or Δp, or u) is:

$$\varepsilon - \varepsilon_0 = \left(\frac{\partial\varepsilon}{\partial\varrho}\right)_0 \Delta\varrho + \frac{1}{2}\left(\frac{\partial^2\varepsilon}{\partial\varrho^2}\right)_0 (\Delta\varrho)^2.$$

---

*As will be shown below, energy or intensity of sound is proportional to square of amplitude of changes of pressure or density. Loudness of sound is measured in decibels, in logarithmic scale. As zero is taken average threshold of sensitivity of the human ear. Increase of loudness by n decibels signifies increase of energy of sound by $10^{n/10}$ times. Increase of loudness from rustle of leaves or whisper (~10 db) to orchestra fortissimo (~80 db) corresponds to increase of energy of sound by 10^7 times.

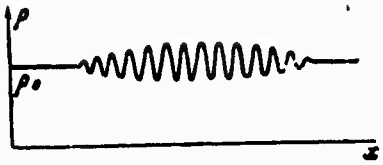

Fig. 1.3. Distribution of density in a wave packet.

By virtue of adiabaticity of motion, derivatives are taken at constant entropy. It is possible to calculate them with help of thermodynamic relationship: $d\varepsilon = T\,dS - p\,dV = (p/\rho^2)\,d\rho$.

We will obtain

$$\varepsilon - \varepsilon_0 = \frac{p_0}{\rho_0^2}\,\Delta\rho + \frac{c^2}{2\rho_0^2}(\Delta\rho)^2 - \frac{p_0}{\rho_0^3}(\Delta\rho)^2.$$

Increase of internal energy in 1 cm^3 with the same accuracy is equal to

$$\rho\varepsilon - \rho_0\varepsilon_0 = (\rho_0 + \Delta\rho)(\varepsilon - \varepsilon_0) + \varepsilon_0\,\Delta\rho = \left(\varepsilon_0 + \frac{p_0}{\rho_0}\right)\Delta\rho + \frac{c^2}{2\rho_0}(\Delta\rho)^2 = w_0\Delta\rho + \frac{c^2}{2\rho_0}(\Delta\rho)^2,$$

where $w = \varepsilon + p/\rho$ is specific enthalpy.

Density of internal energy connected with the perturbation, in the first approximation is proportional to $\Delta\rho$. Density of kinetic energy $\rho u^2/2 \approx \rho_0 u^2/2$ is a quantity of the second order of smallness. From relationship (1.33), which holds for a plane travelling wave, it is clear that the term of the second order in internal energy density and the kinetic energy are exactly equal to each other, so that total energy density of perturbation is

$$E = w_0\,\Delta\rho + \frac{c^2}{2\rho_0}(\Delta\rho)^2 + \frac{\rho_0 u^2}{2} = w_0\Delta\rho + \rho_0 u^2. \qquad (1.36)$$

Term of first order of smallness in energy is connected with change of volume of all of the gas which occurred as a result of the perturbation. If perturbation was created in such a way that volume of gas on the whole was not changed, then energy of perturbation of all of the gas is a quantity of the second order with respect to $\Delta\rho$, since during integration over volume, the term proportional to $\Delta\rho$ vanishes.

Such, for instance, is the situation in a wave packet which propagates through gas occupying an infinite space, where at infinity the gas is not perturbed (Fig. 1.3). Changes of density in regions of compression, with accuracy up to terms of the second order are compensated by changes in regions of rarefaction.

Thus, energy of sound is a quantity of the second order of smallness which is proportional to square of amplitude:*

$$E_{3B} = \rho_0 u^2. \tag{1.37}$$

If perturbation was created in such a way that volume of gas was changed, then in energy of perturbation there remains a term which is proportional to first power of Δρ. However, this main fraction of energy, which is proportional to Δρ, may be "returned by the gas," if source of perturbation returns to its own initial position. Energy then remaining in the perturbed gas will constitute only a quantity of the second order of smallness. Let us explain this situation in a simple example.

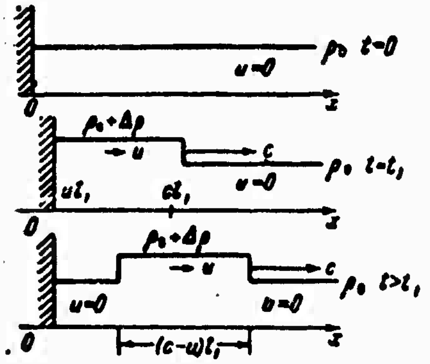

Fig. 1.4. Propagation of impulse of compression from piston which was thrust into gas.

Let us assume that at the initial moment, into the gas at rest there began to be thrust a piston with constant velocity u (much smaller than speed of sound u << c). At time t_1, the piston "instantaneously" stops. Through the gas will travel a pulse of

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*Expression (1.37) should be averaged over time or space:

$$E_{3B} = \rho_0 \overline{u^2} \; (\bar{u} \sim \overline{\Delta\rho} \sim \overline{\Delta p} = 0, \text{ while } \overline{u^2} \sim (\overline{\Delta\rho})^2 \sim (\overline{\Delta p})^2 > 0).$$

compression of length $(c - u)\ t_1 \approx ct_1$, whose energy is equal to work expended by the external force which pushed the piston in, $put_1 = (p_0 + \Delta p)\ ut_1 \approx p_0 ut_1$ (this case was considered above and is illustrated by Fig. 1.4). Energy in first approximation is proportional to "amplitude" of wave u, $\Delta\rho$, Δp and time of compression (i.e., length of the perturbation). Let us now give the gas the possibility to return the piston to its place in such a way that at time t_1, velocity of piston u "instantaneously" changes to the opposite, $(-u)$, and at the time $t_2 = 2t_1$, the piston, which has returned to the initial position, "instantaneously" stops. Perturbation will now have the form depicted in Fig. 1.5, where there are shown states at moments $t = 0$, t_1, t_2 and $t > t_2$. It is easy to verify by direct calculation that in the second period, from t_1 to t_2, the gas performed on the piston work which in first approximation is exactly equal to work which was accomplished by piston on the gas in the first period from zero to t_1. Lengths of positive and negative regions of the pulse in first approximation are also identical and are equal to $ct_1 = c(t_2 - t_1)$. Thus, if we sum the energies in compressed and rarefied regions of the pulse, then terms of first order will cancel out. If we carry out all calculations taking into account terms of following order,* then in the energy there will remain term of the second order, where perturbation energy density will be expressed by general formula (1.37).

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*In particular, lengths of pulses of compression and rarefaction will differ by the amount $2ut_1$ (for $t_2 - t_1 = t_1$).

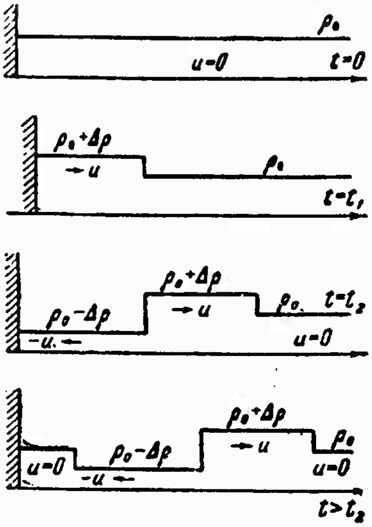

Fig. 1.5. Propagation of pulses of compression and rarefaction from a piston which was first thrust into gas, and then returned to its original place.

§ 4. Spherical Sound Waves

In absence of absorption (i.e., without taking into account viscosity and thermal conduction; see § 22), amplitude and density of energy of plane waves do not decrease with flow of time. For instance, pulses depicted in Fig. 1.4 and 1.5 depart to "infinity," without changing their shape and amplitude.

In spherical wave this is no longer so. By linearizing equation of continuity in the spherically symmetric case, we will obtain

$$\frac{\partial \Delta\varrho}{\partial t} = -\frac{\varrho_0}{r^2}\frac{\partial}{\partial r}r^2u.$$

Linearized equation of motion does not differ from (1.28):

$$\frac{\partial u}{\partial t} = -\frac{c^2}{\varrho_0}\frac{\partial \Delta\varrho}{\partial r}.$$

Hence, as in the plane case, we will obtain wave equation for $\Delta\rho$, solution of which, which describes the wave going out from the center, is

$$\Delta\varrho = \frac{f(r-ct)}{r}. \qquad (1.38)$$

If we consider short pulses, of length much less than r, then it is possible to say that shape of pulse given by function $f(r - ct)$ does not change, and amplitude of wave decreases proportionally to $1/r$. This is fully natural. Let us assume that from the center there proceeds a pulse of finite width Δr. With propagation of the pulse, the mass of substance involved in motion, which is equal approximately to $\rho_0 4\pi r^2 \Delta r$, increases proportionally to r^2. Acoustical energy of unit of volume is proportional to $(\Delta\rho)^2$. Inasmuch as it is conserved, then $(\Delta\rho)^2 r^2 = \text{const}$, i.e., amplitude should decrease as $\Delta\rho \sim 1/r$.

Spherical wave differs from a plane wave in yet one more respect. Let us substitute solution (1.38) in equation of motion:

$$\frac{\partial u}{\partial t} = -\frac{c^2}{\rho_0}\left[\frac{f'(r-ct)}{r} - \frac{f(r-ct)}{r^2}\right],$$

and integrate obtained expression over time. We will obtain solution for velocity:

$$u = \frac{c}{\rho_0}\left[\frac{f(r-ct)}{r} - \frac{\int^{r-ct} f(\xi)\,d\xi}{r^2}\right] = \frac{c}{\rho_0}\left[\Delta\rho - \frac{\varphi(r-ct)}{r^2}\right], \qquad (1.39)$$

which differs from formula for plane case (1.33) by the presence in it of an additional term. In the plane wave in region of perturbation, the substance can be only compressed, as this occurs in the case depicted in Fig. 1.4. In a spherical wave this is impossible: behind the region of compression there necessarily follows a region of rarefaction.

Indeed, behind the region of perturbation, $\Delta\rho$ and u become zero. In the plane case, in virtue of proportionality $u \sim \Delta\rho$, this condition is satisfied automatically, independently of shape of pulse. In spherical wave, for this it is necessary that behind region of perturbation $\varphi(r - ct) = 0$, i.e., that integral over entire region of perturbation is equal to zero

$$\varphi(r-ct) = \int f(\xi)\,d\xi = \int r\,\Delta\rho\,dr = 0.$$

Hence it is clear that $\Delta\rho$ in spherical wave changes sign, i.e., behind region of compression there follows a region of rarefaction.

Additional quantity of substance contained in wave is equal to $\int \Delta\rho \cdot 4\pi r^2 dr$. But $\Delta\rho \sim 1/r$; therefore additional mass in compressional wave increases as wave goes out from the center. The quantity of compressed substances increasing in process of propagations causes the appearance of a wave of lowered density following behind the wave of raised density.

Change of pressure in spherical wave is proportional to change of density, as in the plane wave. Velocity, as can be seen from formula (1.39), is not proportional to $\Delta\rho$ or Δp. In particular, velocity and change of density change sign at various points, so that in a wave propagating from the center, profiles of density and speed have the form depicted in Fig. 1.6.

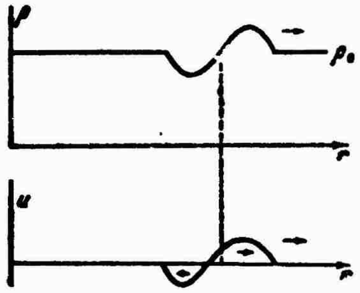

Fig. 1.6. Distribution of density and velocity in spherical sound wave.

§ 5. Characteristics

In § 3 it was shown that if at initial moment t_0 at some point x_0 of motionless gas whose density and pressure everywhere are identical, we create arbitrary small perturbations of velocity and pressure (or density*), then from this point in both directions with speed of sound there travel two waves carrying the perturbations. In the wave propagating in the direction of positive x,

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*In virtue of isentropic character of flow, changes of density and pressure are not independent, but always are related to each other by the thermodynamic relationship $\Delta p = c^2 \Delta p$.

to the right, small changes of all quantities are related with each other by the relationships:

$$\Delta_1 u = \frac{\Delta_1 p}{\rho_0 c} = \frac{c}{\rho_0} \Delta_1 \rho = f(x - ct) \, .^*$$

In wave, propagating to the left:

$$\Delta_2 u = -\frac{\Delta_2 p}{\rho_0 c} = -\frac{c}{\rho_0} \Delta_2 \rho = -f_2 (x + ct).$$

Arbitrary perturbations Δu and Δp, which appear at initial moment, can always be broken-up into two components: $\Delta u = \Delta_1 u + \Delta_2 u$, $\Delta p = \Delta_1 p + \Delta_2 p$, which obey these relationships, so that, in general, initial perturbation is propagated in different directions in the form of two waves.

If initial perturbations Δu, Δp are not arbitrary, but already are related to each other by one of the relationships, then the perturbation travels in one of the directions (this corresponds to vanishing of one of the functions f_1 or f_2).

If gas is not at rest, but moves as a whole with constant velocity u, then the picture does not change, with only the exception that now the waves are carried by the flow, so that velocities of their propagation relative to a motionless observer become equal to $u + c$ (to the right) and $u - c$ ("to the left"**). This can easily be verified if we go over in equations of gas dynamics to a new system of coordinates moving together with the gas at velocity u.

Let us assume now that in arbitrary plane isentropic flow of gas, described by functions $u(x, t)$, $p(x, t)$ (or $\rho(x, t)$, see first footnote on page 23), at the time t_0 at point x_0 there appeared

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*We write here Δu instead of u for the purpose of consistency of designations.

**We enclose the word "to the left" in quotes: if $u > c$, then the wave also travels to the right, but, of course, slower than the first.

arbitrary small perturbations of velocity and pressure. Considering small region near point x_0 and small intervals of time (small neighborhood of point x_0, t_0 on x, t plane), it is possible in first approximation to disregard changes of unperturbed functions u(x, t), p(x, t), and consequently, ρ(x, t) and c(x, t) in this neighborhood, and to consider them to be constant and equal to values at point x_0, t_0. The entire above described picture of propagation of perturbations can be transferred to this case. If perturbations $\Delta u(x_0, t_0)$, $\Delta p(x_0, t_0)$ are arbitrary, then they also are broken up into two components, one of which will start to propagate to the right with velocity $u_0 + c_0$, and the other "to the left" with velocity $u_0 - c_0$, whereby u_0 and c_0 here one should understand local values of these quantities at point x_0, t_0.

Inasmuch as u and c change from point to point, then for a long period of time, paths of propagation of perturbations on x, t-plane, which are described by equations dx/dt = u + c and dx/dt = u - c will be curved. These lines on x, t-plane along which small perturbations propagate are called characteristics. During plane isentropic flow of gas, as we can see, there exist two families of characteristics, which are described by equations

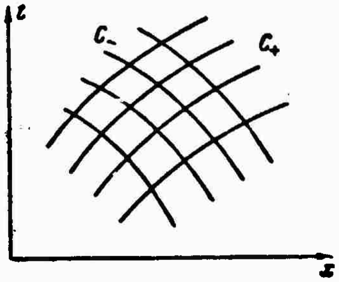

Fig. 1.7. Network of two families of characteristics in the isentropic case.

$$\frac{dx}{dt} = u + c, \quad \frac{dx}{dt} = u - c,$$

and are called respectively C_+- and C_--characteristics.

Through every point on the x, t-plane it is possible to draw two characteristics, which belong to C_+- and C_--families. In general, characteristics are curvilinear, as is shown in Fig. 1.7.

In region of constant flow, where u, p, c, ρ are constant in space and time, characteristics of both families are straight lines.

If flow is not isentropic, but only adiabatic, i.e., if entropies of different particles of gas do not change in time, but differ from each other, there are possible perturbations of entropy. In virtue of adiabatic character of motion, $dS/dt = 0$, i.e., any perturbation of entropy not accompanied by perturbations of other quantities (p, ρ, u) remains localized in the particle and moves together with the particle along the flow line. Flow lines, consequently, in case of non-isentropic flow also are characteristics. They are described by equation $dx/dt = u$ and are called C_0-characteristics.

In non-isentropic flow, through every point x, t there pass three characteristics, and the x, t-plane is covered with a network of three families of characteristics C_+, C_-, C_0 (Fig. 1.8).

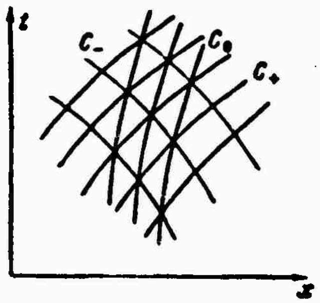

Fig. 1.8. Network of three families of characteristics in the non-isentropic case.

Till now we have spoken about characteristics as lines on the x, t-plane along which small perturbations propagate. However, this does not exhaust the significance of characteristics.

Equations of gas dynamics can be transformed to such a form that they contain derivatives of gas-dynamic quantities only along characteristics. As will be shown in the following section, in isentropic flow, along characteristics there move not only small perturbations, but also definite combinations of gas-dynamic quantities.

As it is known, a function of two variables $f(x, t)$ can be differentiated with respect to time along a definite curve $x = \varphi(t)$ on the x, t-plane. Time derivative of function $f(x, t)$ along arbitrary curve $x = \varphi(t)$ is determined by slope of tangent to curve at given point $dx/dt = \varphi'$ and is equal to

$$\left(\frac{df}{dt}\right)_{\varphi} = \frac{\partial f}{\partial t} + \frac{\partial f}{\partial x}\frac{dx}{dt} = \frac{\partial f}{\partial t} + \frac{\partial f}{\partial x}\varphi'.$$

We are already acquainted with two particular cases of differentiation along a curve: these are the partial derivative with respect to time $\partial/\partial t$ (along curve $x = \text{const}$, $\varphi' = 0$) and particle derivative $d/dt = \partial/\partial t + u\,\partial/\partial x$ (along path of motion of particle or along flow line: $dx/dt = \varphi' = u$).

Let us transform equations of plane adiabatic motion to a form such that they contain derivatives of gas-dynamic quantities only along characteristics. For this we will eliminate from equation of continuity

$$\frac{d\rho}{dt} + \rho\frac{\partial u}{\partial x} = 0$$

the derivative of density, replacing it by derivative of pressure. Inasmuch as density is thermodynamically related to pressure and entropy $\rho = \rho(p, S)$, and $dS/dt = 0$, we have

$$\frac{d\rho}{dt} = \left(\frac{\partial\rho}{\partial p}\right)_S \frac{dp}{dt} + \left(\frac{\partial\rho}{\partial S}\right)_p \frac{dS}{dt} = \frac{1}{c^2}\frac{dp}{dt}.$$

By substituting this expression into the continuity equation and multiplying the equation by c/ρ, we will find

$$\frac{1}{\rho c}\frac{\partial p}{\partial t} + \frac{u}{\rho c}\frac{\partial p}{\partial x} + c\frac{\partial u}{\partial x} = 0.$$

We will add this equation with the equation of motion

$$\frac{\partial u}{\partial t} + u\frac{\partial u}{\partial x} + \frac{1}{\rho}\frac{\partial p}{\partial x} = 0.$$

We obtain

$$\left[\frac{\partial u}{\partial t} + (u + c)\frac{\partial u}{\partial x}\right] + \frac{1}{\rho c}\left[\frac{\partial p}{\partial t} + (u + c)\frac{\partial p}{\partial x}\right] = 0.$$

By subtracting one equation from the other, we will find analogously

$$\left[\frac{\partial u}{\partial t}+(u-c)\frac{\partial u}{\partial x}\right]-\frac{1}{\rho c}\left[\frac{\partial p}{\partial t}+(u-c)\frac{\partial p}{\partial x}\right]=0.$$

The first of these equations contains derivatives only along C_+-characteristics, and the second — only along C_--characteristics. Noticing that adiabatic equation $dS/dt = 0$ can be considered as an equation along C_0-characteristics, we will write equations of gas dynamics in the form

$$du+\frac{1}{\rho c}dp=0 \quad \text{along } C_+:\frac{dx}{dt}=u+c, \tag{1.40}$$

$$du-\frac{1}{\rho c}dp=0 \quad \text{along } C_-:\frac{dx}{dt}=u-c, \tag{1.41}$$

$$dS=0 \quad \text{along } C_0:\frac{dx}{dt}=u. \tag{1.42}$$

In Lagrange coordinates, equations of characteristics take the form

$$C_+:\frac{da}{dt}=c; \quad C_-:\frac{da}{dt}=-c; \quad C_0:\frac{da}{dt}=0.$$

Equations along characteristics do not differ from equations (1.40) to (1.42).

In spherically symmetric flow, equations of characteristics in Euler coordinates are the same as in the plane case (only coordinate x must be replaced by radius r). Equations along characteristics $C_\pm$ contain additional terms depending on the functions themselves, and not on their derivatives

$$du\pm\frac{1}{\rho c}dp=\mp\frac{2u}{r}dt \quad \text{along } C_\pm:\frac{dr}{dt}=u\pm c.$$

In a number of cases, equations of gas dynamics written in characteristic form are more convenient for numerical integration than usual equations.

§ 6. Plane Isentropic Flow. Riemann Invariants

In isentropic flow, entropy, which is constant in space and time, in general drops out of equations. All flow is described by two functions: by velocity u(x, t) and by some one of the thermodynamic variables: $\rho(x, t)$, $p(x, t)$ or $c(x, t)$. The latter are uniquely related with each other at every point by purely thermodynamic relationships: $\rho = \rho(p)$, $c = c(\rho)$ or $p = p(\rho)$, $c = c(\rho)$; $c^2 = dp/d\rho$.

Differential expressions $du + dp/\rho c$ and $du - dp/\rho c$ now constitute total differentials of quantities

$$\left.\begin{aligned} J_+ &= u + \int \frac{dp}{\rho c} = u + \int c \frac{d\rho}{\rho}, \\ J_- &= u - \int \frac{dp}{\rho c} = u - \int c \frac{d\rho}{\rho}, \end{aligned}\right\} \qquad (1.43)$$

which are called Riemann invariants.* With the help of thermodynamic relationships, integral quantities $\int dp/\rho c = \int c \, d\rho/\rho$ in principle can be expressed in terms of one of the thermodynamic variables, let us say, the speed of sound c. For instance, in an ideal gas with constant heat capacity

$$p = \text{const}\, \rho^{\gamma}, \quad c^2 = \gamma \, \text{const}\, \rho^{\gamma-1}$$

and

$$J_{\pm} = u \pm \frac{2}{\gamma - 1} c. \qquad (1.44)$$

Riemann invariants are determined with accuracy up to the arbitrary constant, which in those cases when it is convenient can be completely omitted, as this is done in formula (1.44).

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*During non-isentropic flow, ρ and c depend on two variables: p and S, and the expressions $du \pm dp/\rho c$ no longer are total differentials. Combinations (1.43) in this case do not have a definite meaning.

Equations (1.40), (1.41) indicate that in isentropic flow, Riemann invariants are constant along characteristics

$$\left.\begin{aligned} dJ_+=0, \quad J_+=\text{const along } C_+: \frac{dx}{dt}=u+c; \\ dJ_-=0, \quad J_-=\text{const along } C_-: \frac{dx}{dt}=u-c. \end{aligned}\right\} \tag{1.45}$$

This situation can be considered as generalization of relationships which are accurate for the case of propagation of acoustic waves through a gas with constant velocity, density and pressure. The latter are obtained from general equations as a first approximation. If we assume that $u = u_0 + \Delta u$, $p = p_0 + \Delta p$, then in first approximation

$$J_\pm = u_0 + \Delta u \pm \int \frac{d\Delta p}{\rho_0 c_0} = \Delta u \pm \frac{\Delta p}{\rho_0 c_0} + \text{const.} \tag{1.46}$$

Equations of characteristics in first approximation are written in the form

$$\frac{dx}{dt} = u_0 \pm c_0, \quad x = (u_0 \pm c_0)t + \text{const.}$$

Thus, along path $x = (u_0 + c_0)t$ + const there is kept the quantity $\Delta u + \Delta p/\rho_0 c_0$, from which it is clear that it can be represented in the form of a function of the constant in equation $x = (u_0 + c_0)t +$ + const:

$$\Delta u + \frac{\Delta p}{\rho_0 c_0} = 2f_1[x-(u_0+c_0)t].$$

Along path $x = (u_0 - c_0)t$ + const there is kept the quantity

$$\Delta u - \frac{\Delta p}{\rho_0 c_0} = -2f_2[x-(u_0-c_0)t].$$

Changes of velocity and pressure are represented in the form of superposition of two waves f_1 and f_2, which travel in opposite directions: $\Delta u = f_1 - f_2$, $\Delta p = \rho_0 c_0(f_1 + f_2)$, where in each of them quantities are related to each other by relationships already known to us:

$$\Delta_1 u = \frac{\Delta_1 p}{\rho_0 c_0} = f_1, \quad \Delta_2 u = -\frac{\Delta_2 p}{\rho_0 c_0} = -f_2.$$

Riemann invariants J_+ and J_- can be considered as new functions describing motion of gas in exchange for old variables: velocity of gas u and one of thermodynamic quantities, for instance, speed of sound c. They are uniquely related to variables u and c by equations (1.43). By solving these equations for u and c, it is possible to return from functions J_+, J_- to functions u and c. For instance, for an ideal gas with constant heat capacity, by formulas (1.44)

$$u=\frac{J_++J_-}{2};\quad c=\frac{\gamma-1}{4}(J_+-J_-).$$

Considering invariants as functions of independent variables x and t, equations of characteristics can be written in the form

$$C_+:\frac{dx}{dt}=F_+(J_+,\ J_-);\quad C_-:\frac{dx}{dt}=F_-(J_+,\ J_-), \tag{1.47}$$

where F_+ and F_- are known functions, whose form is determined only by thermodynamic properties of the substance.

In an ideal gas with constant heat capacity

$$F_+=\frac{\gamma+1}{4}J_++\frac{3-\gamma}{4}J_-;\quad F_-=\frac{3-\gamma}{4}J_++\frac{\gamma+1}{4}J_-.$$

As can be seen from equations (1.45), characteristics have the property to transfer constant values of one of the invariants. Inasmuch as along a definite C_+-characteristic J_+ = const, change of slope of characteristic is determined by change of only one quantity – the invariant J_-. In exactly the same way, along the C_--characteristic J_- is constant, and change of slope during transition from one point of the x, t-plane to another is determined by change of invariant J_+.

Equations written in characteristic form make the casual relationship of phenomena in gas dynamics very graphic. Let us consider any plane isentropic flow of gas in an infinite space. Let us assume that at initial moment t = 0 there are given distributions of gas-dynamic quantities over coordinate x: u(x, 0); c(x, 0), or, which is equivalent, there are given distributions of invariants $J_+ (x, 0)$; $J_- (x, 0)$. On the plane of x, t (Fig. 1.9) there exists a network of C_+- and C_--characteristics, which go out from different points of the x-axis.* Values of gas-dynamic quantities at any point D(x, t) (at coordinate point x at the moment of time t) are determined only by values of quantities at initial points $A(x_1, 0)$ and $B(x_2, 0)$:

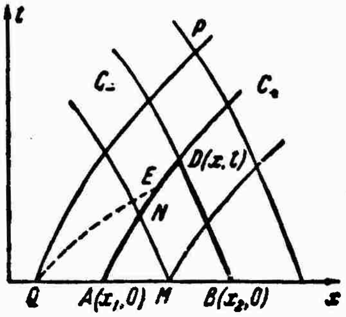

Fig. 1.9. x — t-diagram, illustrating region of dependence.

$$J_+(x, t) = J_+(x_1, 0); \quad J_-(x, t) = J_-(x_2, 0).$$

For instance, for an ideal gas with constant heat capacity, by solving these equations for u and c, it is possible to write physical variables at point D in explicit form:

$$\left.\begin{aligned} u(x, t) &= \frac{u_1+u_2}{2} + \frac{2}{\gamma-1}\,\frac{c_1-c_2}{2}, \\ c(x, t) &= \frac{c_1+c_2}{2} + \frac{\gamma-1}{2}\,\frac{u_1-u_2}{2}, \end{aligned}\right\} \qquad (1.48)$$

where u_1, c_1 are values at point $A(x_1, 0)$, and u_2, c_2 are values at point $B(x_2, 0)$.

It is impossible, of course, to say that state of gas at point D depends on assignment of initial conditions only at two initial points A and B, since the actual position of point D, as the place where C_+- and C_--characteristics, going out from points A and B intersect, depends on path of these characteristics. These paths are determined by assignment of initial conditions on all of segment AB of axis x. For instance, slope of C_+-characteristic AD at intermediate point N (see Fig. 1.9) is determined not only by invariant $J_+ (A)$, but also by value of invariant $J_- (M)$, which is transferred to N from intermediate point M of segment AB.

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*It is possible to construct this network after there is found the solution of the problem.

But state of gas at D is completely determined by assignment of initial conditions on segment AB of axis x, and absolutely does not depend on initial values of quantities outside of this segment. If, let us say, we somewhat change initial values at point Q, then this in no way will affect state of gas at D, simply because perturbation due to this change will not succeed in reaching coordinate point x by the moment t. It will arrive at this coordinate point later (at point P along C_+-characteristic QP).

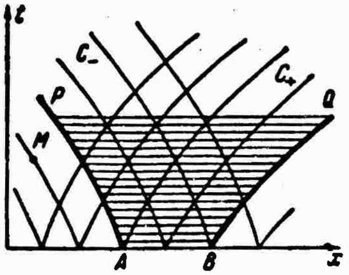

Fig. 1.10. x — t-diagram illustrating region of influence.

Analogously, initial state of gas on segment AB of axis x affects state of gas at subsequent moments of time only at those points which are located inside region bounded by C_--characteristic AP and C_+-characteristic BQ (Fig. 1.10). It does not affect state at M, since "signals" from initial conditions on segment AB will not succeed in reaching coordinate point x_M by moment t_M.

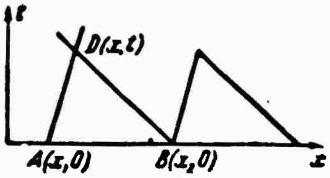

Fig. 1.11. Straightening of characteristics on small sections.

We will stress that the presented considerations about causal relationship of phenomena are valid only under the condition that characteristics of one family do not intersect with each other. For instance, if C_+-characteristic from Q (see Fig. 1.9) went along dotted path QE, then state of gas at Q would influence state at D. But in region of continuous flow, characteristics belonging to one family indeed never intersect. Intersection would lead to non-single-valuedness of gas-dynamic quantities. Indeed, at point of intersection of two C_+-characteristics x, t, invariants J_+ would have two different values, corresponding to each of the two characteristics. Meanwhile, to every point of plane x, t there belongs only one value each of J_+ and J_-, which are related with the unique values of velocity of gas and speed of sound at this point. As we will see below, intersection of characteristics of one family leads to disturbance of continuity of flow and appearance of discontinuities of gas-dynamic quantities, i.e., shock waves.

It is possible to draw lines of characteristics on all of plane x, t only if we know solution of gas-dynamic problem. If solution is unknown, then it is impossible to indicate exactly the position of point D in Fig. 1.9 at which characteristics going out from A and B intersect.

However, it is possible approximately to find place of intersection by replacing true curvilinear paths AD and BD by straight lines whose slopes correspond to initial values of u_1c_1; u_2c_2 at points A and B (or J_+ (A), J_- (B)) (Fig. 1.11). Selecting points A and B sufficiently close to each other in such a manner that error due to replacement of true paths of characteristics by straight lines is small, we find position of point of intersection from equations

$$x - x_1 = (u_1 + c_1)\,t, \quad x - x_2 = (u_2 - c_2)\,t.$$

Values of u and c at place of intersection are determined by formulas (1.48). Such an operation, in essence, constitutes the simplest scheme of numerical integration of equations (1.45). Covering plane x, t by a network of triangles analogous to ADB, it is possible successively, step by step, to advance solution of equations forward in time, proceeding from initial conditions u(x, 0), c(x, 0) or J_+ (x, 0), J_- (x, 0).

§ 7. Plane Isentropic Flow of Gas in a Bounded Space

Let us consider some plane isentropic flow of gas in a bounded space. Let us assume that the gas occupies space between two plane surfaces — pistons, which move according to given laws $x_1 = \psi_1 (t)$, $x_2 = \psi_2 (t)$, where at initial moment $t = 0$ coordinates of pistons are equal to x_{10} and x_{20}. At initial moment there are given distributions of velocity u and thermodynamic variable c over coordinate x on segment $x_{10} < x < x_{20}$: $u(x, 0)$, $c(x, 0)$ or, which is equivalent, there are given distributions of invariants $J_+ (x, 0)$, $J_- (x, 0)$.

Let us draw on plane x, t a network of characteristics and lines of pistons (Fig. 1.12). Points of type F, through which there pass C_+- and C_--characteristics going out from points lying inside segment $0_1 0_2$ of axis x do not at all differ from points during motion of gas in unbounded space. Just as there, to these points there are transferred initial values of invariants J_+ and J_-.

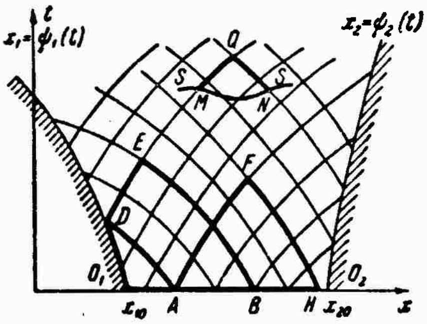

Fig. 1.12. Scheme of characteristics for plane isentropic flow of gas between two pistons.

We will consider a point lying on line of piston, for definiteness, point D of the left piston.

To point D from the "past" there is transferred only one invariant J_-; it is transferred along the C_--characteristic coming from point A of initial segment $0_1 0_2$ so that $J_-(D) = J_-(A)$. Second invariant J_+ is not brought to D, since C_+-characteristic does not arrive at D (from the "past"). C_+-characteristic only goes out from D (into the "future"), taking with it the value of invariant J_+ "formed" at this point.

State of gas at point D is determined by value of introduced invariant J_- and a second quantity — velocity u, which in virtue of boundary condition coincides with known velocity of piston at point D: $u_1(D)$. This pair of quantities $J_-(D) = J_-(A)$ and $u = u_1(D)$ replaces now the pair of quantities J_+, J_-, which arrive at points of gas, which do not touch the pistons. Second invariant J_+ is composed in D of quantities $J_-(D)$ and $u_1(D)$: $J_+(D) = 2u_1(D) - J_-(D)$, and is transferred by the C_+-characteristic. For instance, to point E arrives C_--characteristic going out from point B of initial segment of x-axis and carrying invariant $J_-(B)$: $J_-(E) = J_-(B)$. C_+-characteristic arrives from line of piston, from D, and brings invariant J_+, which is equal to $J_+(D)$: $J_+(E) = J_+(D)$.

State of gas at E depends on initial conditions on segment O_1B of axis x and velocities of left piston on segment O_1D of line of piston.

Thus, during flow in bounded space, state of gas at any point may depend not only on initial conditions, but also on boundary conditions.

In general, the state at arbitrary point of plane x, t is determined by assignment of values of u and c or J_+, J_- on segment of arbitrary curve cut off by C_+- and C_--characteristics passsing through the considered point. For instance, state at Q is determined by state on segment MN of curve S (see Fig. 1.12).

Analogously to the preceding, onto the right piston from the "past" along C_+-characteristics are transferred invariants J_+, and C_--characteristics themselves start from points of line of piston and carry into the "future" invariants J_-, which are composed of the introduced invariants J_+ and values of velocity of piston u_2, with which velocities of layer of gas adjacent to piston coincide.

Pressure on piston is uniquely determined by the one introduced invariant and velocity of piston. Let us consider for example point D on left piston. Let us assume that gas is ideal with constant heat capacity. Let us designate by u_A, c_A initial velocity of gas and speed of sound at point A, and by u_{1D} velocity of piston at point D. We have for speeds of gas and sound at D

$$u_D = u_{1D}, \quad J_- = u_D - \frac{2}{\gamma-1} c_D = u_A - \frac{2}{\gamma-1} c_A,$$

whence

$$c_D = c_A + (u_{10} - u_A)\frac{\gamma-1}{2}$$

or in terms of the invariant

$$c_D = [u_{10} - J_-(A)]\frac{\gamma-1}{2}.$$

Pressure on piston p_D is related with speed of sound c_D purely thermodynamically, $p_D = \text{const}\ c_D^{2\gamma/(\gamma-1)}$.

Presented considerations permit us to give graphic physical meaning to Riemann invariants.

Let us take the following experiment: Let us introduce at a definite moment t at point x a flat plate parallel to surface of piston. Let us assume that on one, the left side of the plate there is a pressure indicator, which reacts to pressure of gas on the left of the plate.

By moment t at x from the left onto the indicator there arrives invariant $J_+ = u + \int dp/\rho c = u + w(p)$, where u and p are velocity and pressure of gas unperturbed by the plate (w(p) is function of pressure, depending only on thermodynamic properties of gas and its entropy). At the time t, gas is decelerated near plate and stops, inasmuch as the plate is at rest. New pressure on the left of the plate corresponding to the stopped gas (u = 0) we will designate by p_1. Then

$J_+ = u + w(p) = w(p_1)$. Indicator will register pressure of repulsion $-p_1$. Inasmuch as function w is known, scale of indicator can be calibrated in such a manner that reading of indicator directly gives magnitude of invariant J_+. Analogously, pressure indicator placed on right side of plate measures invariant J_- arriving from the right.

If we place a very thin plate perpendicular to surfaces of pistons, parallel to velocity of flow, in such a manner that gas freely flows around the plate without changing velocity, the indicator will register pressure of unperturbed flow p. Since it is calibrated to directly give magnitude of w(p), the indicator will measure combination of invariant

$$w(p) = \frac{1}{2}(J_+ - J_-).$$

§ 8. Simple Waves

From formula (1.46) for Riemann invariants, which pertains to case of propagation of small perturbations, acoustic waves, through gas it is clear that if wave propagates only in one direction, then one of invariants is constant in space and time. Thus, if wave travels to the right and $\Delta u\ (x, t) = \Delta p\ (x, t)/\rho_0 c_0 = f_1\ [x - (u_0 + c_0)\ t]$, then invariant J_- is constant:

$$J_- = \Delta u - \frac{\Delta p}{\rho_0 c_0} + \text{const} = \text{const}.$$

If, however, the wave travels to the left, then invariant J_+ is constant.

We will show that possibility of existence of waves travelling in one direction is not limited by the assumption of smallness of amplitude, where in the general case of a travelling wave there remains constant one of the Riemann invariants. First of all we will indicate how it is possible to realize in practice constancy of one of the invariants, for instance J_-. If gas occupies an infinite space, then for this it is sufficient to assign initial distributions u(x, 0), c(x, 0) in such a way that at initial moment we had $J_-(x, 0) = \text{const}$. Inasmuch as this constant value of J_- is transferred along C_--characteristics going out from all points of axis x, then at subsequent moments of time invariant J_- will remain constant: $J_-(x, t) = \text{const}$.

Let us assume that gas occupies a half-space bounded on the left by piston moving according to the law $x_1 = \psi_1(t)$. If at initial moment $J_-(x, 0) = \text{const}$ in all of the region occupied by gas, $x > x_{10}$ (x_{10} is initial coordinate of piston), then at subsequent moments J_- also will remain constant in the whole space bounded by the piston $x > x_1 = \psi_1(t)$. Actually, left piston, as was shown in preceding paragraph, "excites" only C_+-characteristics; C_--characteristics arrive at line of piston from "past", and on this "finish their existence", so that piston sends into the "future" only J_+-invariants, but not J_-.

Values of J_--invariants in all that part of plane x, t which corresponds to gas (this part is bounded by line of piston $x_1 = \psi_1(t)$) are determined by initial values of J_- on axis x, i.e., are constant.

Conversely, if gas occupies half-space bounded on the right by piston (line of piston $x_2 = \psi_2(t)$, $x_{20} = \psi_2(0)$), and at initial moment $J_+(x, 0) = \text{const}$ for $x < x_{20}$, then in the whole physical part of plane x, t, $x < x_2 = \psi_2(t)$, invariant J_+ is constant.

Thus, we will return to problem at hand and will assume for definiteness that $J_-(x, t) = \text{const}$.

From equation of characteristics written in form (1.47), it follows thus that C_+-characteristics constitute a family of straight lines (F_+ = const, since J_+ = const along the characteristic, and J_- = const in general). Integrating equation for C_+-characteristics, we will write

$$x = F_+(J_+, J_-)t + \varphi(J_+), \tag{1.49}$$

where $\varphi(J_+)$ is constant of integration, which it is possible to consider as function of that value of J_+ which is transferred along the characteristic. It is determined by initial and boundary conditions of the problem. For instance, if given characteristic emerges from initial segment of axis x, then φ is coordinate of that point of axis x from which there emerges the characteristic and on which there is assigned value of J_+ standing as the argument in φ.

Formula (1.49), jointly with condition imposed on one of the unknown functions,

$$J_-(x, t) = \mathrm{const}, \tag{1.50}$$

constitutes general solution of equations of gas dynamics for the considered case. It determines in implicit form the other unknown function $J_+(x, t)$. (We recall that function F_+ is known, inasmuch as there are known the thermodynamic properties of the substance).

Solution (1.49), (1.50) can be written in the form of formulas for usual gas-dynamic variables: velocity of gas and speed of sound. From equation (1.50)

$$J_- = u - \int \frac{dp}{\varrho c} = \mathrm{const}$$

it follows that speed of sound or any otner thermodynamic variable, let us say pressure, are functions of velocity n which do not contain in explicit form independent variables x and t: $c = c(u)$, $p = p(u)$.

Equation (1.49) is equivalent to equation

$$x=[u+c(u)]t+\varphi(u), \tag{1.51}$$

where constant of integration φ is expressed as a function of u. This equation determines in implicit form u in dependence upon x and t.

From formula (1.51) it is clear that given values of u and c(u) are transferred through the gas along axis x with constant velocity u + c(u). In other words, the solution constitutes a wave travelling to the right:

$$u=f\{x-[u+c(u)]t\},\quad c=g\{x-[u+c(u)]t\},$$

where form of functions f and g is determined by initial and boundary conditions of the problem.

However, in distinction from travelling wave of small amplitude, different values of velocity of gas and thermodynamic variables are transferred with different velocities, so that initial profiles u(x, 0), c(x, 0) are distorted with flow of time. This is a result of the nonlinearity of equations of gas dynamics.

The obtained solution in the form of a travelling wave is called a simple wave.

In an analogous way there can be obtained a simple wave travelling in the other direction. In it invariant J_+ is constant, and C_--characteristics are straight lines. General solution in this case has the form

$$J_+=\text{const},\quad x=F_-(J_+,\ I_-)t+\varphi_1(J_-)$$

or

$$J_+=u+\int\frac{dp}{\rho c}=\text{const},\qquad x=[u-c(u)]t+\varphi_1(u),$$

$$u=f_1\{x+[c(u)-u]t\},\quad c=g_1\{x+[c(u)-u]t\}.$$

Let us note that solution for simple wave is particular solution of equations of one-dimensional isentropic flow. There can be found also the general solution of these equations for arbitrary flow (see [1]). Singular solution is not contained directly in the general solution.

§ 9. Distortion of Profiles in Travelling Wave of Finite Amplitude. Certain Properties of Simple Waves

We will use obtained solution for a simple wave and will clarify what occurs with a wave of acoustic type if we do not limit ourselves to first approximation, as this was done in § 3, but start from the exact equations of gas dynamics. We will not give here an analytic solution, but will clarify qualitative character of phenomena with the help of graphic construction. Gas will be considered to be ideal with constant heat capacity.

Let us assume that initial profiles of velocity and speed of sound $u(x, 0)$, $c(x, 0)$ have form depicted in Fig. 1.13, where these functions are related in such a way that $J_-(x, 0) = \text{const}$ (we consider a wave travelling to the right). By formula (1.44) we have $c = \frac{\gamma-1}{2} u + c_0$, where constant value of invariant J_- is selected in accordance with the condition that in unperturbed gas $u = 0$, $c = c_0$. Inasmuch as $p \sim c^{2/(\gamma-1)}$, $\rho \sim c^{2\gamma/(\gamma-1)}$ (for $c = c_0$, $p = p_0$, $\rho = \rho_0$), profiles of pressure and density in qualitative sense are fully analogous to profile of speed of sound.

Being constant at initial moment, invariant $J_-(x, t)$ is constant also at all subsequent moments of time, so that motion constitutes a simple wave travelling to the right. Characteristics of C_+-family are straight lines $dx/dt = u + c = (\gamma + 1) u/2 + c_0$. They are depicted in Fig. 1.13. From points A_0, B_0 and D_0, where $u = 0$, they emerge parallel to each other: $dx/dt = c_0$ (and parallel to C_+-characteristics going out from points of axis x which correspond to unperturbed region of gas). In order not to complicate Fig. 1.13, we will draw, furthermore, only two more C_+-characteristics, from points E_0 and F_0, which correspond to minima and maxima of initial distributions $u(x, 0)$ and $c(x, 0)$.

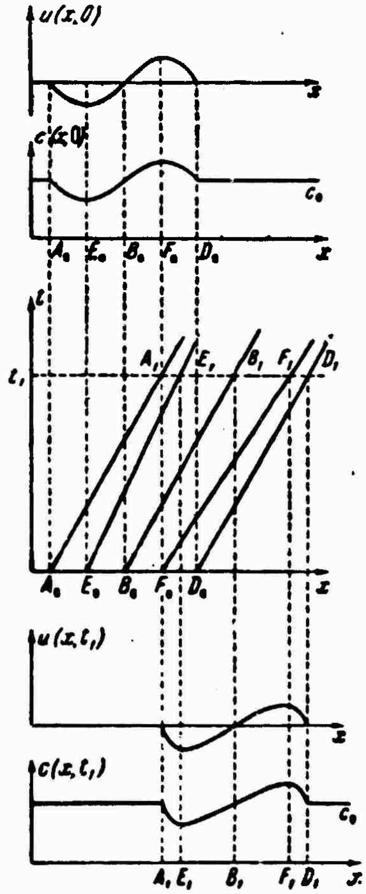

Fig. 1.13. Propagation of travelling wave to the right. Construction allowing us to determine distortion of profiles in wave. Above — profiles of velocity and speed of sound at initial moment. Below — distorted profiles at time t_1. In the middle — scheme of C_+-characteristics.

Let us construct profiles of u and c at moment t_1: $u(x, t_1)$, $c(x, t_1)$. Inasmuch as along C_+-characteristics there are transferred constant values of u and c, magnitudes of u and c at points A_1, E_1, etc., are equal to corresponding magnitudes at points A_0, E_0, etc.

By performing the construction as shown in Fig. 1.13, we will find profiles of u and c at time t_1. We see that "head" (D) and "tail" (A) of the wave, which touch regions of constant flow, where $u = 0$, and $c = c_0$, were displaced along axis x by segments equal to c_0t_1 (they were propagated along characteristics D_0D_1, A_0A_1 on plane x, t). Heights of maxima and minima of u and c were not changed, but relative positions of maxima and minima became different: profiles were distorted.

In acoustic theory, where equations of gas dynamics are linearized, such distortion does not occur: profiles shift in the form of a "frozen" picture. Distortion of profiles is result of nonlinearity of equations of gas dynamics. Physical cause of distortion is that wave crests travel relatively faster due to high speed of their propagation through substance (high speed of sound), as well as due to faster drift forward together with the substance (high speed of gas). Conversely, wave troughs travel relatively slower, since both speeds in them are less.

With flow of time profiles are distorted more and more strongly, as is shown in Fig. 1.14. If we formally continue the analytic solution to sufficiently long times, then there will occur "overlapping" of the wave, as shown in Fig. 1.14d. This, the last, picture is physically senseless, since in it the solution is not single-valued. For instance, at point $x = x'$ in the same moment of time there are three values of velocity u: $u = 0$, u_1 and u_2. Appearance of such ambiguity is mathematically connected with intersection of characteristics of one family (C_+), the tendency to which it is possible to perceive in Fig. 1.13. In fact, "overlapping" certainly does not occur, and when front and rear parts of profiles become very steep, there are formed discontinuities — shock waves, as shown in Fig. 1.14e (about this we will be concerned below).

Thus, solution in the form of simple wave in this case is valid only for a limited time, up to moment of formation of discontinuities. Solution never loses validity only in that case when wave everywhere has character of a wave of rarefaction, i.e., does not contain sections where velocity of gas, pressure, and density decrease in direction of propagation of wave. Such sections (AE and FD) in Fig. 1.13 constitute compressional waves.

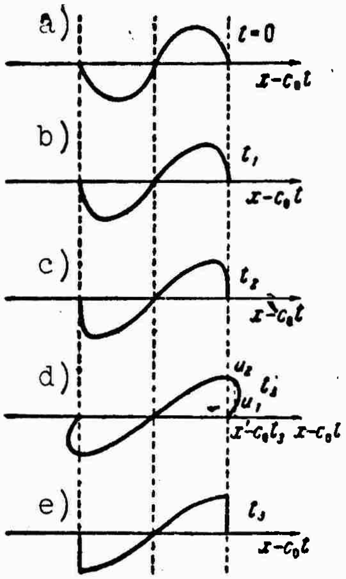

Fig. 1.14. Diagram illustrating build-up of steepness and "overlapping" of wave of finite amplitude in nonlinear theory. There are shown profiles of velocity in consecutive moments of time. In order to combine waves at different moments of time, along the axis of abscissas is plotted the combination $x-c_0t$. Profile d) corresponds to the physically unreal state. In fact, at time t_3 the profile has the form e) with discontinuities.

Simple rarefaction wave will be considered in the following section.

Let us note one important property of the simple wave which is illustrated by the considered example. Head of simple wave always is propagated along the characteristic (in our example along characteristic D_0D_1). On the leading edge of the simple wave, at point D, the actual quantities u and c are continuous, but their derivatives with respect to coordinate x undergo a discontinuity (this one may see from Fig. 1.13, where profiles of u and c undergo a break). Such a singularity, in which quantities are continuous but their derivatives are discontinuous is called weak. Weak singularity can be imagined as a small perturbation with respect to continuous variation of gas-dynamic quantities. This is shown in Fig. 1.15, in which there are depicted two profiles, one smoothed, and the other with discontinuity of derivative. The shaded section can be considered as a small perturbation.

But we know that small perturbations are propagated through a substance with speed of sound. Therefore, weak singularities always are propagated along the characteristics.

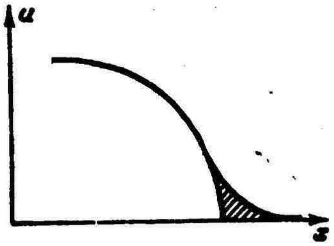

Fig. 1.15. Concerning the question of a weak singularity.

If isentropic flow borders with region of constant flow, then this flow necessarily is a simple wave, and, conversely, with region of constant flow there can border only a simple wave. Actually, in region of constant flow C_+- and C_--characteristics constitute families of parallel lines, and invariants J_+ (x, t) and J_- (x, t) are constant. As boundary of contact of region of some isentropic flow I with region of constant flow II (Fig. 1.16) serves one of characteristics, let us say, the C_+-characteristic. Then C_--characteristics continuing from region II into region I transfer constant value of J_-, so that in region I J_- (x, t) = const. Consequently, this region is a simple wave travelling to the right. In Fig. 1.16 there are drawn characteristics for case of a pulse with length of one "wave length", which was considered above as an example.

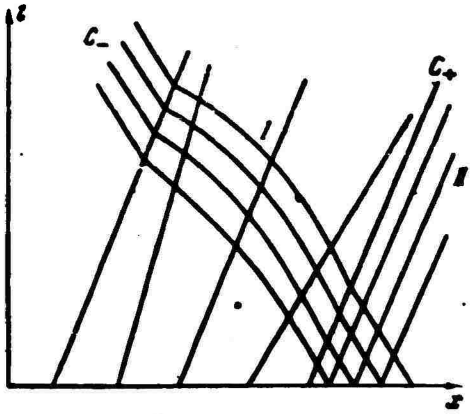

Fig. 1.16. Diagram of two families of characteristics for the wave depicted in Fig. 1.13.

§ 10. Rarefaction Wave

Let us consider motion of gas under action of a withdrawing piston. Let us assume that in the beginning a motionless gas with constant density, pressure, and speed of sound ρ_0, p_0, c_0 occupies half-space $x > 0$, on the left bounded by motionless piston, initial coordinate of which is $x = 0$. At the time $t = 0$, piston starts to move to the left, gradually being accelerated from zero speed to a certain constant speed, which we will designate by $-U$. Law of motion of piston is $x = X(t)$. When speed of piston becomes constant, line $X(t)$ becomes a straight line $X(t) = -Ut + \text{const}$.

As was shown in the preceding section, motion of gas for $t > 0$ constitutes a simple wave travelling to the right. Head of wave, i.e., initial perturbation from piston, propagates to the right with speed of sound along C_+-characteristic OA; $x = c_0 t$ (Fig. 1.17). Let us draw on this figure curve of motion of piston $X(t)$ and characteristics of C_+- and C_--families. In region I between axis x and C_+-characteristic OA, gas is undisturbed: characteristics in this region are straight lines with slopes $(dx/dt)_+ = c_0$; $(dx/dt)_- = -c_0$. After intersecting straight line OA, C_--characteristics continue up to line of piston and on it end their existence. For clarity of reasoning, we will consider gas to be ideal with constant heat capacity; however, we will stress that in a qualitative sense the entire picture of motion remains valid also for gas with different thermodynamic properties. J_--invariant is constant in the entire physical part of plane x, t and is equal

$$J_- = u - \frac{2}{\gamma-1}c = -\frac{2}{\gamma-1}c_0.$$

Hence,

$$u = -\frac{2}{\gamma-1}(c_0 - c), \quad c = c_0 + \frac{\gamma-1}{2}u.$$

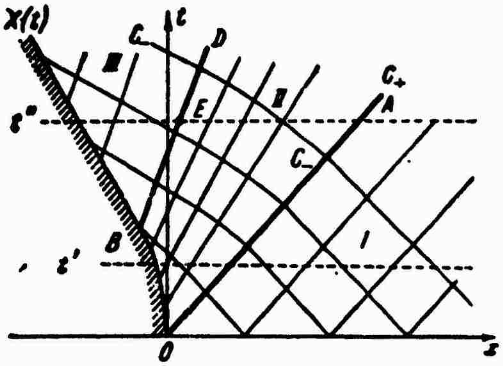

Fig. 1.17. x, t-diagram with diagram of characteristics for rarefaction wave appearing under action of piston which is withdrawn from gas, first accelerated, and then with constant speed.

On boundary with piston, velocity of gas coincides with velocity of piston w(t), which is negative. Therefore, speed of sound, and also pressure and density of gas at the piston are less than initial, and the faster the piston travels, the lower they are. C_+-characteristics, which are straight lines, emerge from line of piston with slopes

$$\left(\frac{dx}{dt}\right)_+ = u + c = c_0 + \frac{\gamma+1}{2}u = c_0 - \frac{\gamma+1}{2}|w|.$$

Inasmuch as piston only is accelerated, but not decelerated, C_+-characteristics starting on line of piston only diverge, but nowhere converge, as is shown in Fig. 1.17. C_+-characteristics going out from that section of line of piston on which speed of piston is already constant have identical slopes $(dx/dt)_+ = c_0 - \frac{\gamma+1}{2}U$ and go in parallel with each other. Let us assume that, for instance, speed of piston becomes strictly constant and equal to $w = -U$ $(U > 0)$, starting from moment t_1 (point B on line of piston). In region III on plane x, t, which is contained between line of piston and C_+-characteristic BD, all gas-dynamic quantities are constant: $u = -U$, $c = c_0 - \frac{\gamma - 1}{2} U = c_1$*). Indeed, in this region J_- = const in virtue

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*For validity of these formulas it is necessary that c_1 be a positive quantity, which puts a limitation on final velocity of piston: $U < [2/(\gamma - 1)]\, c_0$. The case when $U > \frac{2}{\gamma - 1} c_0$ will be considered in § 11.

of general constancy, and J_+ = const inasmuch as velocities of gas on line of piston, from which there emerge all C_+-characteristics, are identical:

$$J_+ = u + \frac{2}{\gamma-1}c = \frac{2}{\gamma-1}c_0 + 2u = \frac{2}{\gamma-1}c_0 - 2U.$$

In region II, which is contained between C_+-characteristics OA and BD and section OB of line of piston, gas-dynamic quantities depend on x and t in accordance with solution for simple wave. C_+-characteristics going out from section OB of line of piston at all later moments of time carry smaller and smaller values of velocities of sound and gas (greater and greater velocities of gas in absolute value). Therefore, distribution of u and c over the gas at some definite moment of time $t' < t_1$, which corresponds to horizontal line t = const = t' on plane x, t, has the form depicted in Fig. 1.18a.

In virtue of direct dependence of p, ρ and c, distributions of density and pressure in a qualitative sense are similar to distribution of speed of sound.

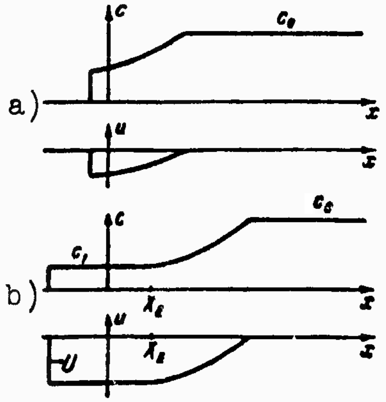

Fig. 1.18. Profiles of speed of sound and velocity in rarefaction wave appearing under action of piston (see Fig. 1.17): a) up to moment when speed of piston became constant, $t' < t_1$; b) after moment when speed of piston became constant, $t'' > t_1$.

Distributions of gas-dynamic quantities at later moment $t'' > t_1$ (straight line t = const = t" on plane x, t) are shown in Fig. 1.18b. In this case to the piston is adjoined region of constant flow u = -U, $c = c_1$. Coordinate of point dividing regions of constant and variable flows III and II corresponds to point E of characteristic BD: x_E.

By assigning a specific law of motion to the piston, we can find solution of problem in analytic form. Let us assume, for example, that speed of piston with flow of time changes smoothly according to the law:

$$w = -U\left(1 - e^{-\frac{t}{\tau}}\right), \quad \tau > 0$$

and tends to constant -U asymptotically as t → ∞. Line of motion of piston is described by equation

$$X(t) = \int_0^t w\,dt = -U\tau\left[\frac{t}{\tau} - \left(1 - e^{-\frac{t}{\tau}}\right)\right].$$

It asymptotically passes into straight line $X = -U(t - \tau)$.

For finding the unknown solution we will subject the general solution (1.51) to boundary condition: $u = w(t)$ when $x = X(t)$. This condition determines arbitrary function $\varphi(u)$:

$$\varphi(w) = X(t) - [w + c(w)]\,t,$$

where

$$c(w) = c_0 + \frac{\gamma - 1}{2} w \quad \text{and} \quad w = w(t).$$

Substituting here X (t) and expressing time in terms of w with help of law of motion of piston $t = -\tau \ln\left(1 + \frac{W}{U}\right)$, we will find form of function φ:

$$\varphi(w) = -w\tau + \tau\left(c_0 + \frac{\gamma+1}{2} w + U\right) \ln\left(1 + \frac{w}{U}\right).$$

Distributions of velocity over coordinate at different moments of time are given by implicit function:

$$x = \left(c_0 + \frac{\gamma+1}{2} u\right) t - u\tau + \tau\left(c_0 + \frac{\gamma+1}{2} u + U\right) \ln\left(1 + \frac{u}{U}\right),$$

which holds in the interval $X(t) < x < c_0 t$.

Let us assume again that velocity of piston becomes strictly constant at definite moment t_1. Let us take the constant value of final velocity of the piston -U and assume that initial accelerations of piston become greater and greater and constant velocity is attained more and more rapidly ($t_1 \to 0$). Section OB of line of piston, where speed of piston is variable, becomes smaller and smaller (see Fig.

1.17). Points B and O, from which C_+-characteristics BD and OA, between which is contained the region of variable flow II, go out, thus come closer together. In the limit $t_1 = 0$, when points B and O coincide, which corresponds to instantaneous attainment by piston of constant velocity $w = -U$, both characteristics BD and OA emerge from one point: from the origin of coordinates $x = 0$, $t = 0$ on plane x, t. All C_+-characteristics filling the region of variable flow II also emerge from origin O in the form of a fan. Thus, in the limiting case, when piston at time $t = 0$ starts to move with constant speed $w = -U$, the picture on plane x, t acquires the form depicted in Fig. 1.19.

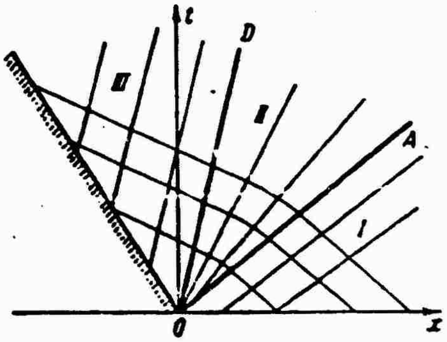

Fig. 1.19. x, t-diagram with diagram of characteristics for centered rarefaction wave.

All characteristic lines: line of "head" of rarefaction wave OA, line of "tail" of wave OD, behind which parameters of gas take constant finite values, and line of piston emerge from "center" O. From the same "center" there emerge all C_+-characteristics located between C_+-characteristics OA and OD.

Such a wave is called a centered simple wave. Inasmuch as all C_+-characteristics in centered simple wave, i.e., in region of variable flow II, emerge from point $x = 0$, $t = 0$, function $\varphi(u)$ in solution (1.51); which is at the same time the equation of these characteristics, becomes zero. Solution for centered wave has the form

$$x = [u + c(u)]\,t. \tag{1.52}$$

Formally this solution can be obtained by means of passage to the limit $\tau \to 0$ in the example, considered above. Function φ is proportional to τ, so that as $\tau \to 0$ $\varphi(u) \to 0$.

Let us write in explicit form the solution for centered rarefaction wave for case of ideal gas with constant heat capacity. Relation of thermodynamic variables with velocity of gas u is given by the already known formula following from condition of constancy of invariant J_-:

$$c = c_0 - \frac{\gamma-1}{2}|u|, \quad u < 0. \qquad (1.53)$$

Inasmuch as $p = p_0 (\rho/\rho_0)^\gamma$, $c^2 = \gamma p/\rho = c_0^2 (\rho/\rho_0)^{\gamma-1}$,

$$\rho = \rho_0 \left[1 - \frac{\gamma-1}{2}\frac{|u|}{c_0}\right]^{\frac{2}{\gamma-1}}, \qquad (1.54)$$

$$p = p_0 \left[1 - \frac{\gamma-1}{2}\frac{|u|}{c_0}\right]^{\frac{2\gamma}{\gamma-1}}. \qquad (1.55)$$

In order to obtain dependence of these quantities on x and t, it is necessary to substitute here $|u|$, which is found from solution of (1.52) and (1.53):

$$|u| = \frac{2}{\gamma+1}\left(c_0 - \frac{x}{t}\right). \qquad (1.56)$$

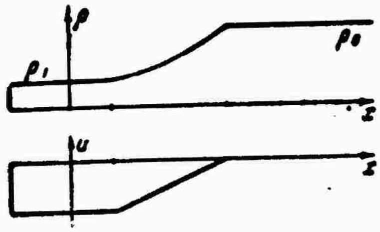

Fig. 1.20. Profiles of density and velocity in centered rarefaction wave.

Velocity of gas in centered rarefaction wave depends on coordinate x by a linear law. Head of wave, where u = 0, moves along line $x = c_0 t$; tail of wave, where $u = w = -U$, moves along line $x = (c_1 - U)t = (c_0 - \frac{\gamma+1}{2} U)t$.

Profiles of density and velocity are shown in Fig. 1.20.

§ 11. Centered Rarefaction Wave as an Example of Self-Similar Motion of Gas

One-dimensional plane motion of gas considered in preceding section, which appears during withdrawal of piston with constant velocity, possesses one characteristic peculiarity. All gas-dynamic quantities describing motion, u (x, t), c (x, t), ρ (x, t), p (x, t), depend not separately on coordinate and time, but only in combination x/t. For region II, where quantities are variable, this may be seen directly from formulas (1.53) — (1.56). Regions of constant flow I and III, however, are bounded in plane x, t by straight lines $x/t = c_0 = \text{const}$ (region I) and $x/t = w = \text{const}$, $x/t = w + c_1 = \text{const}$ (region III), which are described by equations containing x and t only in combination x/t. In other words, with flow of time, distributions of all quantities over coordinate x, which are depicted in Fig. 1.20, only are extended in space, without changing their shape, i.e., they remain similar to themselves. If we depict distributions of u, c, ρ, p, plotting along the axis of abscissas not x, but the ratio x/t (or one of the dimensionless quantities x/c_0t, x/wt), then we will obtain a "frozen" picture, which is constant in time. Such motion, in which profiles of gas-dynamic quantities with flow of time remain similar to themselves, changing only due to change of scales of quantities (in this case of scale of length c_0t or wt), is called self-similar. In § 25 we met with a more complicated example of self-similar motion, in which not only scales of length change, but also scales of gas-dynamic quantities themselves, where self-similar variable ξ has the more general form $\xi = xt^{\alpha}$, where $\alpha = \text{const}$. The above considered centered rarefaction wave constitutes simplest case of self-similar motion, in which $\alpha = -1$, $\xi = x/t$, and scales of gas-dynamic quantities remain constant: with flow of time their profiles u (x, t), c (x, t) self-similarly are extended only along the axis of abscissas, but are not changed along the axis of ordinates (scales of u, c, ρ, p remain constant).

Physical cause of self-similar character of centered rarefaction wave can be explained by using dimension considerations.

If we disregard dissipative processes of viscosity and thermal conduction, then equations of gas dynamics, just as formulas, describing thermodynamic properties of a substance, do not contain any characteristic lengths and times. The only scales of length and time for a gas are the mean free path and mean free time of molecules, with which there are connected the coefficients of viscosity and thermal conductivity. However these scales can characterize only microprocesses occurring at distances and during times corresponding to mean free path and time of molecules, but not macroscopic motions. Matter possesses the dimensional parameter speed of sound, which is contained along with velocity of substance in description of gas-dynamic flows. Thus, if initial and boundary conditions of problem do not contain characteristic lengths and times, motion can depend on coordinate and time taken only in combination, x/t, which has the dimension of velocity.

Such is the considered problem about rarefaction wave appearing under action of piston withdrawn from gas with constant velocity w. Initial and boundary conditions introduce only scales of velocity: c_0 and w (and, of course, scales of density ρ_0 and pressure p_0, but not scales of length or time)*.

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*If velocity of piston is not constant, but depends on time, then immediately there appear scales of time or length. Thus the problem about rarefaction wave ceases to be self-similar: mathematically this follows from formula (1.51): if $\varphi(u) \neq 0$, then u depends on x and t separately. However, if velocity of piston with flow of time becomes constant, as in the example considered in the preceding section, then true solution asymptotically tends to self-similar. For $t \gg \tau$ $(t/\tau \to \infty)$ function $\varphi(u) \sim \tau$ in the solution can be omitted. Physically this corresponds to a case in which for $t \gg \tau$ parameter τ becomes small as compared to characteristic time of problem t, and its role becomes less and less important. For greater detail about asymptotic tendency of true solutions to self-similar solutions (see Chapters X and XII).

Self-similar motions have large importance for gas dynamics. Inasmuch as in this case, gas-dynamic quantities do not depend on coordinates and time separately, but depend only on definite combinations of them, this decreases by one the number of independent variables in the system of equations. In particular, during one-dimensional motions, instead of two variables x and t (or r and t in case of spherical or cylindrical symmetry) there appears one independent variable ($\xi = x/t$ in our problem). Flow is described not by partial differential equations, but by ordinary differential equations, which to a huge degree simplifies problem from the mathematical point of view.

In view of fundamental importance of self-similar flow which constitutes a centered simple wave, we once again will find solution of problem about the piston, starting from general equations of gas dynamics and using the presented considerations about decrease of number of independent variables. We transform Euler equations of gas dynamics to new independent variable $\xi = x/t$. If f (x, t) is a certain function of x and t depending only on a combination of these quantities $\xi = x/t$, then by means of direct calculation we will obtain

$$\frac{\partial f}{\partial x}=\frac{1}{t}\frac{df}{d\xi},$$

$$\frac{\partial f}{\partial t}=-\frac{x}{t^2}\frac{df}{d\xi}=-\frac{\xi}{t}\frac{df}{d\xi},$$

$$\frac{df}{dt}=\frac{\partial f}{\partial t}+u\frac{\partial f}{\partial x}=\frac{u-\xi}{t}\frac{df}{d\xi}.$$

Let us transform equations of continuity, motion and adiabatic equation, written for the plane case, with help of these formulas:

$$\begin{aligned}&\frac{d\varrho}{dt}=-\varrho\frac{\partial u}{\partial x}\rightarrow(u-\xi)\frac{d\varrho}{d\xi}=-\varrho\frac{du}{d\xi},\\&\varrho\frac{du}{dt}=-\frac{\partial p}{\partial x}\rightarrow(u-\xi)\varrho\frac{du}{d\xi}=-\frac{dp}{d\xi},\\&\frac{dS}{dt}=0\rightarrow(u-\xi)\frac{dS}{d\xi}=0.\end{aligned}\qquad(1.57)$$

As we should have expected, actual quantities x and t were eliminated from the equations. Written equations admit first of all the trivial solution u = const, p = const, ρ = const, S = const, which corresponds to motion of homogeneous gas as a whole. For obtaining non-trivial solution we will eliminate from first pair of equations $du/d\xi$, and note that third equation gives S = const,* i.e., that self-similar motion is isentropic.

Replacing in the second of equations (1.57) the derivative of pressure by the derivative of density, $dp/d\xi = (dp/d\rho)\,(d\rho/d\xi) = c^2\, d\rho/d\xi$ (inasmuch as motion is isentropic $dp/d\rho = (\partial p/\partial \rho)_S = c^2$), we will obtain

$$[(u-\xi)^2 - c^2]\frac{d\rho}{d\xi} = 0,$$

whence

$$u-\xi = \pm c,\quad \xi = \frac{x}{t} = u \mp c. \qquad (1.58)$$

Substituting this relationship in equations (1.57), we will find

$$du \pm c\frac{d\rho}{\rho} = du \pm \frac{dp}{\rho c} = 0$$

or

$$J_\pm = u \pm \int \frac{dp}{\rho c} = \text{const.} \qquad (1.59)$$

We have arrived, thus, to solution of problem about centered rarefaction wave which was already found in preceding section. For wave travelling to the right, we should take lower sign in formulas (1.58), (1.59), and for wave travelling to the left — the upper sign.

As before, the whole picture of flow can be constructed with help of solutions (1.58), (1.59) and trivial solutions u = const, c = const, which also satisfy self-similar equations. Thus it is

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*The assumption about the fact that not $dS/d\xi = 0$, but $u - \xi = 0$ contradicts the first of equations (1.57).

necessary to combine these solutions in such a manner that there is satisfied boundary condition $u = w$ at the piston.

We will dwell on certain peculiarities of rarefaction wave. Character of solution indicates that for its validity it is not at all necessary that the gas extend from the piston to infinitly $x \to \infty$. Until head of rarefaction wave, which travels through unperturbed gas to the right with the speed of sound c_0, reaches the boundary of gas, $x = x_1 > 0$, i.e., up to the moment $t_1 = x_1/c_0$, presence of boundary in no way affects the motion.* Therefore, the obtained solution always describes initial stage of motion of gas during withdrawal of piston, even if the gas occupies a bounded region.

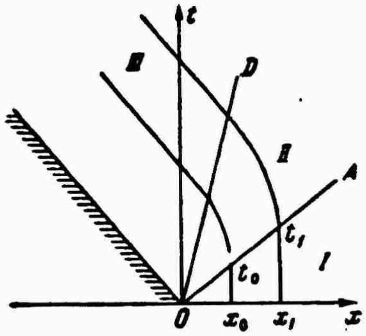

Fig. 1.21. Paths of particles on x, t-diagram for centered rarefaction wave; OA is head of wave, OD is tail of wave.

We will see what happens to a definite particle of gas whose initial coordinate was, let us say, x_0. Up to the moment $t = t_0 = x_0/c_0$, until head of rarefaction wave approaches it, particle is at rest. Then it starts to move to the left, with acceleration, and thus is expanded. When density in it falls to a final value ρ_1, and velocity becomes equal to velocity of piston w, further acceleration and expansion will be ceased, and particle will start to move with constant velocity w. Paths of several particles on plane x, t are depicted in Fig. 1.21. Equations of these lines in region of rarefaction II are easy to obtain by integrating equation for flow line $\frac{dx}{dt} = u = \frac{2}{\gamma - 1}\left(c_0 - \frac{x}{t}\right)$ with initial condition $x = x_0$ for $t = t_0 = \frac{x_0}{c_0}$.

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*Let us remember the reasoning in § 6 about the region of influence.

Let us now see what occurs if we go over to motions with greater and greater absolute velocities of piston $|w|$. From formulas (1.53) – (1.56) it is clear that the greater $|w|$ is, the lower the speed of sound, density, pressure, and temperature $(T \sim \sqrt{c})$ of the gas in the final state ($c_1 = c\ (w)$, $\rho_1 = \rho\ (w)$ etc.) are. Finally, at a certain velocity of the piston $|w|_m = \frac{2}{\gamma - 1} c_0$, final values of c_1, ρ_1, p_1 become zero. If piston is withdrawn still faster, then formally solutions (1.53) – (1.56) become senseless, since for $|u| > |w|_m$ c_1, ρ_1, p_1 are negative.

Actually this means that for $|w| > |w|_m$, between piston and left boundary of gas there will be formed a region of vacuum. Flow proceeds as if piston at initial moment $t = 0$ were completely "removed", and the gas flows into a vacuum. Thus gas is expanded to zero density, pressure, and temperature (speed of sound), and its boundary moves to the left with velocity

$$u = -\frac{2}{\gamma - 1} c_0, \quad |u|_{\max} = \frac{2}{\gamma - 1} c_0. \tag{1.60}$$

Profiles of velocity and density during non-steady outflow into vacuum are depicted in Fig. 1.22. For instance, for air at usual temperatures $\gamma = 7/5$ and $|u|_{\max} = 5c_0$. This magnitude is almost twice as large as velocity of steady outflow into vacuum from a large reservoir, when Bernoulli equation $h + u^2/2 = h_0 = c_0^2/(\gamma - 1)$ is valid, and $u_{\max} = \sqrt{\frac{2}{\gamma - 1}} c_0 \approx 2{,}2\, c_0$ for $\gamma = 1.4$ (here by h we designated specific enthalpy $h = \varepsilon = p/\rho$). During steady outflow, particle obtains kinetic energy of $u^2_{\max}/2$ per gram only due to its initial heat content h_0. During non-steady outflow into vacuum, kinetic energy is larger than its initial heat content h_0 (by more than 4 times at $\gamma = 1.4$).

Additional kinetic energy is obtained due to heat removal from neighboring particles: total energy, which is equal to sum of kinetic and internal energies in region contained in rarefaction wave, is naturally conserved and is equal to initial inertial energy of this region.

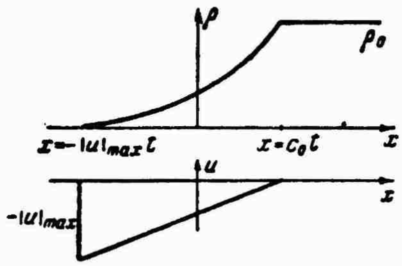

Fig. 1.22. Profiles of density and velocity during plane non-steady outflow of gas into a vacuum.

Analogously to plane case, it is possible to consider spherically or cylindrically symmetric rarefaction waves, which are formed if "spherical" or "cylindrical" pistons at initial moment $t = 0$ start to be withdrawn from the gas occupying space $r > r_0$ or $r < r_0$. Thus there also will be formed a rarefaction wave whose head travels through the undisturbed gas with speed of sound c_0. However, in these cases there do not exist regions of constant flow between piston and tail of rarefaction wave. Let us note that spherical and cylindrical rarefaction wave, in distinction from plane wave, are not self-similar: in the problem there is a characteristic scale of length – the initial radius of the piston r_0.

§ 12. On the Impossibility of Existence of Centered Compressional Wave

It would seem that solution of problem about piston moving with constant speed would be applicable to an equal degree independently of whether piston is withdrawn from gas or is thrust into gas, or whether it produces rarefaction or compression. Both motions are self-similar, i.e., solution for them can be constructed from trivial solutions corresponding to regions of constant flow, and nontrivial solutions corresponding to a simple centered wave. Let us try formally to construct a continuous solution for a self-similar compressional wave which forms if at initial moment piston starts to be thrust into gas with constant speed $w > 0$ (gas is on the right of the piston). "Head" of wave travels through gas with speed of sound c_0 along line $x = c_0 t$ on plane x, t. To the piston is adjacent the region of constant flow, where $u = w$, and $c = c_1$, where both these regions of constant flow (I and III, according to terminology used in the preceding sections) are divided by region of simple centered wave II, where $J_- = u - \frac{2}{\gamma - 1} c = \text{const} = - \frac{2}{\gamma - 1} c_0$. It follows from this that $c_1 = c_0 + \frac{\gamma - 1}{2} w$, so that "tail" of wave travels along line $x = (w + c_1)\, t = (\frac{\gamma + 1}{2} w + c_0)\, t$. Distribution of velocity over coordinate x in region II is described by solution analogous to (1.56):

$$u = \frac{2}{\gamma - 1}\left(\frac{x}{t} - c_0\right).$$

It is obtained that "tail" of wave is propagated faster than "head": $\frac{\gamma + 1}{2} w + c_0 > c_0$, and profiles of velocity and density have form depicted in Fig. 1.23.

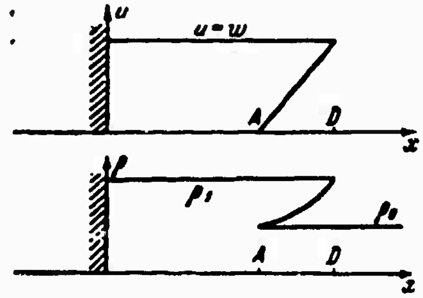

Fig. 1.23. Profiles of velocity and density, corresponding to continuous solution for self-similar (centered) compressional wave. A — head of wave, D — tail of wave. Solution is not single-valued and is physically meaningless.

This picture is physically meaningless; solution is not single-valued in region II. But the obtained solution is the only continuous solution which follows from equations of gas dynamics. Consequently, in this case a continuous solution does not exist. This difficulty historically was one of the starting points for construction of discontinuous solutions of equations of gas dynamics, i.e., for construction of theory of shock waves.

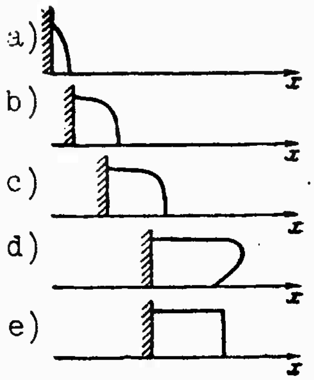

Fig. 1.24. Gradual build-up of steepness of profile of velocity in compressional wave which propagates under action of accelerated piston. d) corresponds to physically meaningless continuous solution with "overlapping" of wave; e) shows actual profile with discontinuity after moment of "overlapping."

Let us note that if piston starts to be thrust into gas not with constant velocity, but gradually, being accelerated from state of rest, then there can be found continuous solution for a simple (but no longer centered) compressional wave, which describes initial stage of motion. The situation in this case is fully analogous to that which exists in sound wave with amplitude which is not small (see § 7). Characteristics of C_+-family (if piston is on the left of the gas) approach each other and tend to intersect, steepness of profile of compressional wave increases with flow of time (as shown in Fig. 1.24), and at a certain moment there occurs "overlapping"; there appears non-single-valuedness of solution analogous to that described in § 7 and in this paragraph. In fact this means that there will be formed a discontinuity — a shock wave.

2. Shock Waves

§ 13. Introduction of Concept of Shock Wave into Gas Dynamics

Let us consider a gas at rest with constant density and pressure ρ_0, p_0 bounded on the left by a plane piston and assume that at initial moment the piston starts to compress gas with constant velocity, which we will now designate by u.

As was shown in the preceding paragraph, an attempt to find continuous solution for this problem leads to a physically meaningless result. Inasmuch as problem is self-similar (does not contain any characteristic scales of length and time), the only solutions satisfying equations of gas dynamics are the trivial solution, in which all quantities u, ρ, p are constant, and a solution of the type of a centered simple wave. Thus, there remains only one possibility to construct a solution satisfying boundary conditions of the problem in an unperturbed gas $u = 0$, $p = p_0$, $\rho = \rho_0$; in region of gas adjacent to piston, speed of gas is equal to speed of piston; this is to discard the physically meaningless region II and to directly join regions of constant flow I and III, assuming that at point of joining, gas-dynamic quantities undergo a discontinuity, as shown in Fig. 1.25.

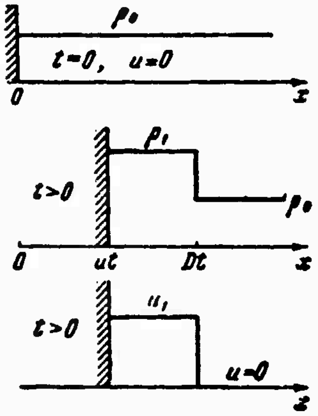

Fig. 1.25. Profiles of density and velocity in shock wave. Wave appears under action of piston, which at initial moment starts to be thrust into gas with constant velocity. On upper figure appears the initial state.

In general, laws of conservation of mass, momentum and energy, which are assumed on the basis of equations of dynamics of inviscid and non-thermally-conducting gas, do not stipulate necessary continuity of gas-dynamic quantities. These laws were formulated earlier in the form of differential equations simply because from the very beginning there was assumed continuity of flow. But these laws can be applied also to regions in which gas-dynamic quantities experience a discontinuity. From the mathematical point of view, it is possible to consider discontinuity as the limiting case of very large gradients of gas-dynamic quantities, when thickness of layer in which there occurs finite change of these magnitudes tends to zero. Inasmuch as in dynamics of inviscid and non-thermally-conducting gas, i.e., under the condition that we disregard molecular structure of the substance, there are no characteristic lengths, and possibilities of existence of as many thin transition layers as desired are not limited. In the limit they reduce to a discontinuity. These discontinuities constitute shock waves.

Let us find the unknown quantities: density and pressure of gas in compressed region ρ_1, p_1, and also velocity of propagation of shock through undisturbed substance D, by proceeding from general laws of conservation of mass, momentum, and energy, whose validity we will not subject to doubt. Parameters of undisturbed gas ρ_0, p_0 and velocity of piston u, which coincides with speed of gas, will be considered to be known. By moment t, in a column with section of 1 cm^2, the motion involves a mass of gas equal to $\rho_0 Dt$. This mass occupies volume (D - u) t, i.e., density of compressed gas ρ_1 satisfies the condition:

$$\rho_1 (D-u) t = \rho_0 Dt.$$

Mass $\rho_0 Dt$ acquires momentum $\rho_0 Dt \cdot u$, which by Newton's law is equal to the impulse of forces of pressure. The resultant force acting on compressed gas is equal to difference between pressures on the side of the piston and on the side of the undisturbed substance, i.e.,

$$\rho_0 Dut = (p_1 - p_0) t.$$

Finally, the increase of sum of internal and kinetic energies of compressed gas is equal to work of external force pushing the piston $p_1 ut$:

$$\rho_0 Dt \left(\varepsilon_1 - \varepsilon_0 + \frac{u^2}{2} \right) = p_1 ut.$$

Cancelling out time t in these equalities, we will obtain a system of three algebraic equations for determination of three unknown quantities

p_1, ρ_1, D in terms of known quantities u, ρ_0, p_0 (thermodynamic relation ε (p, ρ), of course, is assumed to be known).

Let us transform these equations in such a way that in the right sides of equalities there are only quantities pertaining to region before the shock, and in the left sides, parameters of gas behind the shock. For this let us note that if D is speed of propagation of shock through the motionless gas, then $u_0 = -D$ is the speed with which undisturbed gas flows into the shock, and D - u is speed of propagation of the shock relative to gas moving after it, i.e., $u_1 = -(D - u)$ is the speed with which gas flows out of the shock. Introducing these designations into the equations, we will write law of conservation of mass:

$$\rho_1 u_1 = \rho_0 u_0. \tag{1.61}$$

Law of conservation of momentum with help of (1.61) acquires the form

$$p_1 + \rho_1 u_1^2 = p_0 + \rho_0 u_0^2. \tag{1.62}$$

Law of conservation of energy with help of equations (1.61) and (1.62) will be transformed to the form

$$\varepsilon_1 + \frac{p_1}{\rho_1} + \frac{u_1^2}{2} = \varepsilon_0 + \frac{p_0}{\rho_0} + \frac{u_0^2}{2}. \tag{1.63}$$

By introducing specific enthalpy $w = \varepsilon + p/\rho$, we can rewrite it differently:

$$w_1 + \frac{u_1^2}{2} = w_0 + \frac{u_0^2}{2}. \tag{1.64}$$

The obtained equations constitute relationships between gas-dynamic quantities on surface of the discontinuity, into which gas flows in the direction normal to the actual surface, written in the most general form.

It is noteworthy that they do not contain any assumptions about properties of substance and are expressions only of general laws of conservation of mass, momentum, and energy.

Equations (1.61) – (1.63) can be derived directly, by considering the shock in the system of coordinates in which it is at rest. Inasmuch as the shock is infinitely thin, inside it there does not occur accumulation of mass, momentum, and energy. Consequently, fluxes of these quantities on the side of the undisturbed gas are equal to fluxes on the other side of the shock. If into the shock, normal to the surface, there flows gas with density ρ_0 and speed u_0, then flux of mass is $\rho_0 u_0$; it is equal to the mass flowing out through 1 cm^2 in 1 sec on the other side of the shock, i.e., $\rho_1 u_1$. Thus, we obtain equation (1.61). Mass $\rho_0 u_0$ flowing through 1 cm^2 in 1 sec has momentum $\rho_0 u_0 \cdot u_0$. Increase of momentum during transition through the shock $\rho_1 u_1^2 - \rho_0 u_0^2$ is equal to impulse of forces of pressure for 1 sec $p_0 - p_1$ or, which is the same, fluxes of momentum $p + \rho u^2$ on both sides of the shock are equal to each other (the fact that quantity $p + \rho u^2$ is momentum flux density during plane motion is clear from formulas (1.7), (1.8)). Thus there is obtained equation (1.62).

Increase of total (internal and kinetic) energy of gas flowing in 1 sec through 1 cm^2 of surface of shock $\rho_0 u_0\left[\left(\varepsilon_1+\frac{u_1^2}{2}\right)-\left(\varepsilon_0+\frac{u_0^2}{2}\right)\right]$, is equal to work of forces of pressure accomplished in 1 sec from calculation on 1 cm^2 of surface. This work is equal to $p_0 u_0 - p_1 u_1$. In order to explain the origin of this last quantity, we will imagine a pipe through which gas flows from the right to the left through the shock, which is somewhere in between (Fig. 1.26). On the right and on the left in the pipe there are placed pistons, which move with speeds u_0 and u_1 in such a way that surface of discontinuity is at rest. Right piston, to which there is applied pressure p_0, drives the gas through the pipe, accomplishing work $p_0 u_0$ in 1 sec on 1 cm^2.

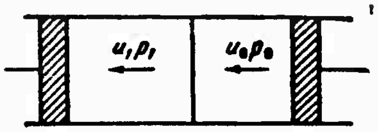

Fig. 1.26. Experiment explaining derivation of expression for work.

On the left piston gas accomplishes work p_1u_1 (piston "accomplishes" on the gas negative work $- p_1u_1$). Thus, the total work accomplished on the gas is equal to $p_0u_0 - p_1u_1$. Equating it to the increase of energy of gas, we will obtain equation (1.63). It is possible to interpret it differently: total fluxes of energy on both sides of the shock $\rho u \left(\varepsilon + \frac{u^2}{2} + \frac{p}{\rho}\right)$, the expression for which follows from energy equation written in form (1.10), are equal to each other.

Formally relationships (1.61) — (1.63), which indicate equality of fluxes of mass, momentum, and energy through surface of the discontinuity, can also be obtained from differential equations (1.2), (1.7), (1.10), which are an expression of the same laws. Let us write these equations for the plane case:

$$\begin{gathered}\frac{\partial \rho}{\partial t} = -\frac{\partial}{\partial x}(\rho u),\\ \frac{\partial}{\partial t}(\rho u) = -\frac{\partial}{\partial x}(p + \rho u^2),\\ \frac{\partial}{\partial t}\left(\rho\varepsilon + \frac{\rho u^2}{2}\right) = -\frac{\partial}{\partial x}\left[\rho u\left(\varepsilon + \frac{u^2}{2} + \frac{p}{\rho}\right)\right].\end{gathered} \qquad (1.65)$$

We will at first formally consider the shock as some thin layer with large gradients of all quantities and will integrate equations over this layer from x_0 to x_1. For instance,

$$\int_{x_0}^{x_1} \frac{\partial}{\partial t}(\rho u)\, dx = -\int_{x_0}^{x_1} \frac{\partial}{\partial x}(p + \rho u^2)\, dx.$$

Now we will carry out passage to the limit, letting thickness of layer $x_1 - x_0$ approach zero. Integrals in left sides, which are proportional to $x_1 - x_0 \to 0$, vanish (which corresponds to absence of accumulation of mass, momentum, and energy in the shock). Integrals in right sides give difference of fluxes of corresponding quantities on both sides of the shock, i.e., we arrive at equations (1.61) – (1.63).

It is necessary to stress the formal character of the last derivation of relationships on the shock wave (1.61) – (1.63). It indicates only that expressions for fluxes of mass, momentum, and energy standing under divergence signs in differential equations are absolutely general, independently of whether the flow is continuous or not. If we consider the shock not as a mathematical surface, but as a thin layer of finite thickness, where gas-dynamic quantities change very sharply, but continuously, then it is impossible to apply to this layer equations (1.65), in which there are not considered viscosity and thermal conduction. Below we will see that entropies of gas on both sides of the shock are different, while in differential equations (1.65) there is imposed the condition of constancy of entropy (adiabatic character of motion). Let us note the external similarity of the energy relationship on the shock wave (1.64) with Bernoulli integral for steady flow

$$w+\frac{u^2}{2}=\text{const},$$

which is valid along the flow line.

§ 14. Shock Adiabat

Equations (1.61) – (1.63), which relate parameters of gas on both sides of the shock, constitute a system of three algebraic equations in six quantities: u_0, ρ_0, p_0, u_1, ρ_1, p_1 (thermodynamic properties of substance, i.e., functions ε (p, ρ) or w (p, ρ) are assumed to be known). Knowing thermodynamic parameters of gas before the shock ρ_0, p_0 and taking one of the quantities which characterize amplitude of shock wave, for instance, pressure after the front of the wave p_1 or speed of "piston" creating the wave $|u| = u_0 - u_1$, it is possible to calculate all remaining unknown quantities. Let us write out certain general relationships which follow from laws of conservation (1.61) – (1.63). Let us introduce in place of densities specific volumes $V_0 = 1/\rho_0$, $V_1 = 1/\rho_1$. From equation (1.61) we will obtain

$$\frac{V_0}{V_1} = \frac{u_0}{u_1}. \qquad (1.66)$$

By eliminating from first two equations (1.61) – (1.62) at first one, and then the other velocity, we will find

$$u_0^2 = V_0^2 \frac{p_1 - p_0}{V_0 - V_1}, \qquad (1.67)$$

$$u_1^2 = V_1^2 \frac{p_1 - p_0}{V_0 - V_1}. \qquad (1.68)$$

If shock wave is created in gas at rest by motion of piston, for the velocity of compressed gas relative to undisturbed gas, which is equal to velocity of the "piston", we will obtain formula

$$|u| = u_0 - u_1 = \sqrt{(p_1 - p_0)(V_0 - V_1)}. \qquad (1.69)$$

We will note a useful formula for difference of kinetic energies of gas on both sides of the shock in system of coordinates in which shock is at rest:

$$\frac{1}{2}(u_0^2 - u_1^2) = \frac{1}{2}(p_1 - p_0)(V_0 + V_1). \qquad (1.70)$$

By substituting expressions for squares of velocities (1.67), (1.68) in energy equation (1.63), we will obtain relationship relating pressure and specific volume on both sides of the shock:

$$\varepsilon_1(p_1 V_1) - \varepsilon_0(p_0 V_0) = \frac{1}{2}(p_1 + p_0)(V_0 - V_1). \qquad (1.71)$$

Replacing specific internal energies by specific enthalpies according to the formula $w = \varepsilon + pV$, we will rewrite this formula in different form:

$$W_1 - W_0 = \frac{1}{2}(p_1 - p_0)(V_0 + V_1). \qquad (1.72)$$

By analogy with the relationship relating initial and final pressures and volumes during adiabatic compression of a substance, expressions (1.71) or (1.72) have the name shock adiabat or Hugoniot adiabat.

Shock adiabat is represented by function

$$p_1 = H(V_1, p_0, V_0), \tag{1.73}$$

which in a number of specific cases, when thermodynamic relations $\varepsilon = \varepsilon\ (p, V)$ are expressed by simple formulas, may be found in explicit form.

Shock adiabat has an essential difference from the usual adiabat (Poisson adiabat in ideal gas with constant heat capacity). Whereas the latter is a one-parameter family of curves $p = P\ (V, S)$, where as the parameter there serves only the value of entropy S, Hugoniot adiabat depends on two parameters: pressure and volume in initial state p_0V_0. In order to exhaust all curves $p = P\ (V, S)$, it is sufficient to go through a one-dimensional series of values of entropy S. In order to exhaust all curves $p = H\ (V, p_0V_0)$, it is necessary to construct an "infinity squared" of curves corresponding to all possible p_0 and V_0.

§ 15. Shock Waves in Ideal Gas with Constant Heat Capacity

Especially simple form is acquired by formulas for shock wave in case of an ideal gas with constant heat capacity. In this example it is conveneient to clarify all basic laws of change of quantities in a shock wave. Let us substitute in equations of shock adiabat (1.71) or (1.72) the relationships

$$\varepsilon = c_V T = \frac{1}{\gamma - 1} pV; \quad w = c_p T = \frac{\gamma}{\gamma - 1} pV. \tag{1.74}$$

This gives us the possibility to find in explicit form the equation of shock adiabat:

$$\frac{p_1}{p_0}=\frac{(\gamma+1)V_0-(\gamma-1)V_1}{(\gamma+1)V_0-(\gamma-1)V_0}. \tag{1.75}$$

For ratio of volumes we will obtain formula:

$$\frac{V_1}{V_0}=\frac{(\gamma-1)p_1+(\gamma+1)p_0}{(\gamma+1)p_1+(\gamma-1)p_0}. \tag{1.76}$$

Ratio of temperatures is equal to

$$\frac{T_1}{T_0}=\frac{p_1V_1}{p_0V_0}. \tag{1.77}$$

With help of (1.76), velocities by the formulas (1.67) and (1.68), can be represented in terms of pressures and initial volume:

$$u_0^2=\frac{V_0}{2}\left[(\gamma-1)p_0+(\gamma+1)p_1\right], \tag{1.78}$$

$$u_1^2=\frac{V_0}{2}\frac{\left[(\gamma+1)p_0+(\gamma-1)p_1\right]^2}{\left[(\gamma-1)p_0+(\gamma+1)p_1\right]}. \tag{1.79}$$

We will clarify in the example of an ideal gas with constant heat capacity certain principles for shock waves. Shock adiabat is a curve on the p, V-plane which passes through point of initial state p_0, V_0.

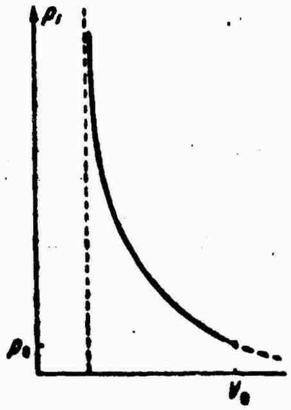

Fig. 1.27. Shock adiabat.

This curve is depicted in Fig. 1.27. In principle, formula (1.75) can also be extended to pressures lower than initial $p_1 < p_0$. As we will see below in § 17, this part of curve corresponds to physically unrealizable states. Therefore, it is drawn in Fig. 1.27 in the form of a dotted line. From formula (1.76), it is clear that in case of shock wave of very high amplitude, when pressure after front is much larger than initial pressure, density of gas during increase of amplitude is increased not without limit, but tends to a definite value. This limiting compression in shock wave depends only on adiabatic index and is equal to

$$\frac{\varrho_1}{\varrho_0}=\frac{V_0}{V_1}=\frac{\gamma+1}{\gamma-1}. \tag{1.80}$$

For a monatomic gas with $\gamma = 5/3$, limiting compression is equal to 4. For a diatomic gas, on the assumption that vibrations are not excited, $\gamma = 7/5$, and limiting compression is equal to 6; if it is considered that vibrations are excited, $\gamma = 9/7$ and compression equals 8. In reality, at high pressures and temperatures, heat capacity and adiabatic index in gases no longer are constants, since in the gas there occur dissociation of molecules and ionization of atoms. Shock adiabat, with consideration of these processes, will be considered in Chapter III. However, even in this case magnitude of compression always remains bounded and does not exceed 11-13. Compression of gas in shock wave at given large pressure ratio is stronger, the higher the heat capacity and the smaller the adiabatic index are.

Inasmuch as at high pressures p_1, density increases very slowly with increase of pressure, temperature of compressed gas increases proportionally to pressure (see formula (1.77) for $V_1 \approx$ const). In the limit of a strong wave, when $p_1/p_0 \gg 1$ and $V_1/V_0 \approx (\gamma - 1)/(\gamma + 1)$,

$$\frac{T_1}{T_0}=\frac{\gamma-1}{\gamma+1}\frac{p_1}{p_0}. \tag{1.81}$$

Velocities in the limit as $p_1/p_0 \to \infty$ increase proportionally to the square root of pressure. As can be seen from formulas (1.67) and (1.68), at $p_1 \gg p_0$,

$$u_0=\sqrt{\frac{\gamma+1}{2}p_1V_0}, \quad u_1=\sqrt{\frac{(\gamma-1)^2}{2(\gamma+1)}p_1V_0}. \tag{1.82}$$

Very important results can be obtained by comparing velocities of gas on both sides of shock with corresponding speeds of sound. In ideal gas with constant heat capacity,

$$c^2=\left(\frac{\partial p}{\partial \varrho}\right)_S=\gamma\frac{p}{\varrho}=\gamma pV.$$

We will form ratios of velocities of gas relative to the shock to speeds of sound:

$$\left(\frac{u_0}{c_0}\right)^2=\frac{(\gamma-1)+(\gamma+1)\frac{p_1}{p_0}}{2\gamma}, \qquad (1.83)$$

$$\left(\frac{u_1}{c_1}\right)^2=\frac{(\gamma-1)+(\gamma+1)\frac{p_0}{p_1}}{2\gamma}. \qquad (1.84)$$

In the limiting case of a shock wave of small amplitude, when pressures on both sides of shock are close to one another, $p_1 \approx p_0$, $(p_1 - p_0)/p_0 \ll 1$, according to the formula (1.76), compression of gas is also small: $V_1 \approx V_0$; speeds of sound are also close to one another $c_1 \approx c_0$. From formulas (1.83) and (1.84), it is clear that in this case $u_0 \approx c_0 \approx c_1 \approx u_1$. But u_0 is velocity of propagation of shock through undisturbed gas. Thus, weak shock wave travels through gas with speed very close to speed of sound, i.e., practically does not differ from an acoustic compressional wave. This is not surprising, since for a small difference of p_1 from p_0, we are dealing with a small perturbation.

Further, from formulas (1.83) and (1.84), it is clear that in a shock wave in which there occurs compression of gas ($V_1 < V_0$, $p_1 > p_0$), gas flows into shock with supersonic velocity $u_0 > c_0$, and flows out of it with subsonic velocity $u_1 < c_1$ (the fact that $V_1 < V_0$, $\rho_1 > \rho_0$ at $p_1 > p_0$ follows from general formulas (1.67), (1.68)). It is possible to say this differently: a shock wave propagates through undisturbed gas with supersonic velocity, and through compressed gas located behind it, it propagates with subsonic velocity. The greater the amplitude of a shock wave, i.e., the greater the ratio p_1/p_0, the higher the speed of the wave front u_0 is as compared to speed of sound in undisturbed gas c_0. Ratio u_1/c_1 in limit of a strong wave $p_1 \gg p_0$ tends to a constant $u_1/c_1 \to \sqrt{(\gamma-1)/2\gamma} < 1$.

We will consider what occurs with entropy of gas during compression of it by a shock wave. Entropy of ideal gas with constant heat capacity with accuracy up to the constant is equal to $S = c_V \ln pV^{\gamma}$. Difference between entropies on each side of shock wave front with help of formula (1.76) can be represented in the form

$$S_1 - S_0 = c_V \ln \frac{p_1 V_1^{\gamma}}{p_0 V_0^{\gamma}} = c_V \ln \left\{ \frac{p_1}{p_0} \left[\frac{(\gamma-1)\frac{p_1}{p_0} + (\gamma+1)}{(\gamma+1)\frac{p_1}{p_0} + (\gamma-1)} \right]^{\gamma} \right\}. \qquad (1.85)$$

In limiting case of a weak wave ($p_1 \approx p_0$), expression in braces is close to unity, and $S_1 \approx S_0$. During growth of amplitude of the wave, i.e., with increase of ratio p_1/p_0, starting from unity, expression in braces, as it is easy to verify, monotonically increases, approaching infinity as $p_1/p_0 \to \infty$. Thus, entropy of gas experiencing shock compression increases — more strongly the higher the amplitude of the shock wave. Growth of entropy indicates that in shock wave there occur irreversible, dissipative processes, which are connected with existence of viscosity and thermal conduction of the substance. A theory in which these processes are not considered naturally cannot describe the actual mechanism of shock compression; it cannot describe the structure of that thin, but in reality finite layer, in which there occurs transition of gas from initial state to final state. Therefore, in the theory in which viscosity and thermal conduction are not taken into account, a shock is a mathematical surface with zero thickness. As was noted above, in such a theory there is no characteristic length which could serve as a scale for thickness of the shock. With consideration of molecular structure of the gas, i.e., processes of viscosity and thermal conduction, such a scale appears. This is the mean free path of molecules, to which coefficients of viscosity and thermal conduction are proportional, and which, in reality, serves as a measure of the actual width of the shock.

It is most significant, however that the actual magnitude of increase of entropy during shock compression absolutely does not depend on mechanism of dissipation, but is determined exclusively by laws of conservation of mass, momentum, and energy. On the mechanism of dissipation depends only width of the shock, i.e., the rate with which irreversible heating of the gas experiencing shock compression occurs. Thus, a glass of hot water must cool to a fully definite room temperature, absolutely independently of the mechanism of heat exchange with its environment, which determines only rate of cooling.

On the mechanism of dissipation there depend values of gradients of gas-dynamic quantities in the transition layer, but not the jumps of these quantities between final and initial states, which are determined only by laws of conservation. For instance, if $\Delta p = p_1 - p_0$ is the pressure jump in a shock wave, and Δx is width of transition layer, then during change of coefficients of viscosity and thermal conduction Δx and $dp/dx \sim \Delta p/\Delta x$ change, but product $\Delta x \frac{dp}{dx} \approx \Delta p$ remains constant. In the limit as coefficients of viscosity and thermal conductivity tend to zero, $\Delta x \rightarrow 0$, and $dp/dx \sim \frac{1}{\Delta x} \rightarrow \infty$, gradients become infinite, which corresponds to a shock wave.

Differential equations of gas dynamics, without taking into account viscosity and thermal conduction, only admit the possibility of existence of shocks, but cannot describe contiuously the transition from initial to final state, since in equations there automatically is imposed the condition of adiabaticity of the process, $dS/dt = 0$, which is equivalent to the equation of energy. Differential equations contain four conservation laws: of mass, momentum, energy, and entropy, while in a shock wave there are satisfied only three of them: all besides the law of conservation of entropy.

To the problem of thickness of front of shock wave, which can be solved only with consideration of the molecular structure of the substance, i.e., with "microscopic" consideration of process of shock compression, we will return below, in § 23. Now we will continue a "macroscopic" description of phenomenon of shock compression using only the laws of conservation of mass, momentum, and energy.

§ 16. Geometric Interpretation of Characteristics of Shock Compression

For best understanding of different features of the theory of a shock wave and properties of the shock adiabat, the graphic constructions in the p, V diagram are very useful. Let us draw on plane of p, V through point A of the initial state of the substance p_0, V_0 a shock adiabat HH (Fig. 1.28). We will consider that character of this curve is analogous to shock adiabat of ideal gas with constant heat capacity, i.e., that the curve everywhere is convex downwards: second derivative d^2p/dV^2 at every point is positive. For the purpose of clarity we will illustrate certain ideas by concrete calculations in the example of an ideal gas with constant heat capacity; however, it is possible to show that these ideas are general and are valid for substances with different thermodynamic properties. The only condition which is imposed on these properties is the condition that shock adiabat at all points be convex downwards. Let us assume that the substance after shock compression passes into state B (p_1, V_1) from state A (p_0, V_0). B(p_1, V_1) is depicted by point B lying on shock adiabat.

By formula (1.67), the velocity of propagation of shock wave through undisturbed substance is given by expression

$$D^2 = u_0^2 = V_0^2 \frac{p_1 - p_0}{V_0 - V_1}.$$

Graphically this velocity is determined by slope of straight line AB, which is drawn from initial state to final state ($(p_1 - p_0)/(V_0 - V_1)$ is equal to tangent of angle of slope of the straight line). From Fig. 1.28 it is clear that the higher the final pressure is (the stronger the shock wave is), the greater the slope of the straight line and the higher the velocity of the wave are. (For illustration, in Fig. 1.28 there are drawn two straight lines, AB and AC).

Let us see what determines initial slope of shock adiabat at point A. Let us calculate derivative dp_1/dV_1 with help of formula (1.75) for an ideal gas with constant heat capacity:

$$\frac{dp_1}{dV_1} = -\frac{(\gamma-1)p_0}{(\gamma+1)V_1-(\gamma-1)V_0} - \frac{p_0[(\gamma+1)V_0-(\gamma-1)V_1](\gamma+1)}{[(\gamma+1)V_1-(\gamma-1)V_0]^2}.$$

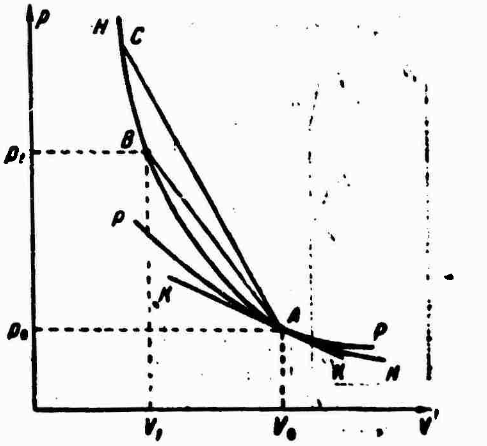

Fig. 1.28. p, V-diagram. HH) Hugoniot adiabat; PP) Poisson adiabat; KK) Tangent to both adiabats at point of initial state A (V_0, p_0).

Taking derivative at point A, i.e., setting $V_1 = V_0$, we will obtain $(dp_1/dV_1)_0 = -\gamma p_0/V_0$. But this quantity is nothing else but slope of Poisson adiabat $p \sim V^{-\gamma}$ passing through point A: $(\partial p/\partial V)_S = -\gamma p/V$. Thus, at point A the shock adiabat touches Poisson adiabat which passes through this point. Usual adiabat P, which corresponds to initial entropy of gas $S_0 = S(p_0 V_0)$, also is drawn in Fig. 1.28. Contact of adiabats at initial point is illustrated also by general formula (1.67) for velocity of shock wave. In the limit of a weak wave, when $(p_1 - p_0)/p_0 \rightarrow 0$, shock wave does not differ from a sound wave, change of entropy tends to zero, and velocity of wave coincides with speed of sound:

$$D^2 = V_0^2 \frac{p_1 - p_0}{V_0 - V_1} \to -V_0^2 \left(\frac{\Delta p}{\Delta V}\right)_S \to c_0^2.$$

In general, slope of straight line AB is always greater than slope of tangent to adiabat at point A, so that we always have $D = u_0 > c_0$.

Initial slope of shock adiabat is determined by speed of sound in initial state. This will be strictly proven for general case of an arbitrary substance in § 18. By direct calculation by the formulas for an ideal gas with constant heat capacity, we can make certain that at point A there coincide not only the first, but also the second derivatives of Hugoniot and Poisson adiabats, i.e., at point A there occurs contact of the second order. This statement also is general (see § 18).

Hugoniot adiabat everywhere passes above the usual adiabat drawn from the initial point, as shown in Fig. 1.28. During shock compression from volume V_0 to volume $V_1 < V_0$, entropy is increased, and during adiabatic compression it remains constant. But, for identical volume, pressure is higher, the greater the entropy.

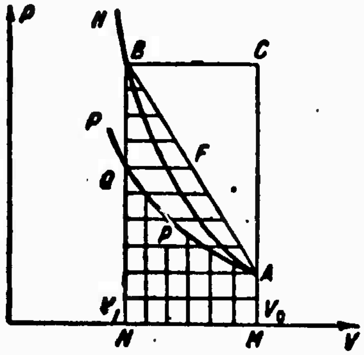

Fig. 1.29. Geometric interpretation of increase of energy in shock wave. H) shock adiabat; P) Poisson adiabat.

Increase of specific internal energy during shock compression from state A to state B, $\varepsilon_1 - \varepsilon_0$, as can be seen from expression (1.71) for the shock adiabat, is numerically equal to area of trapezoid MABN, which is covered in Fig. 1.29 by horizontal shading.

If gas is compressed adiabatically from state A to the very same volume V_1 (to stage Q), then for this it is necessary to accomplish work which is numerically equal to area of figure MAQN, which is bounded above by usual adiabat P and shaded vertically. This area gives increase of internal energy of gas $\varepsilon' - \varepsilon_0 = -\int_{V_0}^{V_1} p\,dV$ (integration is conducted at $S = S_0$). In order to bring gas to final state B, it is necessary to heat it further at constant volume V_1, thereby giving to it a quantity of heat numerically equal to difference between the areas shaded horizontally and vertically, i.e., equal to the area of figure ABQ. This area determines increase of entropy of gas during shock compression. It is equal to $\varepsilon_1 - \varepsilon' = \int_{S_0}^{S_1} T\,dS = \overline{T}(S_1 - S_0)$, where $\overline{T}$ is a certain average temperature on segment of straight line QB (at $V = V_1 = \text{const}$).

In system of coordinates in which initial gas is at rest, after compression it obtains kinetic energy (per gram) equal, according to general formula (1.69), to

$$\frac{u^2}{2} = \frac{(u_0 - u_1)^2}{2} = \frac{1}{2}(p_1 - p_0)(V_0 - V_1).$$

This energy is numerically equal to area of triangle ABC in Fig. 1.29, which completes trapezoid MABN, whose area corresponds to $\varepsilon_1 - \varepsilon_0$, to form rectangle MCBN.

Area of this rectangle $p_1 (V_0 - V_1)$ is total energy given by "piston" to 1 gram of gas initially at rest. In a strong shock wave, when $p_1 \gg p_0$, it is equally divided between increases of internal and kinetic energy: area MABN ≈ area ABC:

$$\varepsilon_1 - \varepsilon_0 \approx \frac{u^2}{2} \approx \frac{1}{2} p_1 (V_1 - V_0).$$

We will analyze on p, V-diagram the relationship between velocities of gas and sound in final state (Fig. 1.30). We will draw through point B on adiabat H_A, which corresponds to initial state A, a new adiabat H_B, for which point B is initial. From the symmetry of equation of adiabat relative to "0" and "1", it follows that if

$p_1 = H(V_1, p_0, V_0)$, then $p_0 = H(V_0, p_1, V_1)$. In other words, adiabat H_B, if formally continued in the direction of pressures smaller than initial, intersects adiabat H_A at point A. The relative location of adiabats H_A and H_B is just as shown in Fig. 1.30, which can be easily checked in the example of an ideal gas with constant heat capacity.* Velocity of propagation of wave relative to compressed gas is determined by formula (1.68)

$$u_1^2 = V_1^2 \frac{p_1 - p_0}{V_0 - V_1}.$$

Square of speed of sound in compressed gas at point B is equal to

$$c_1^2 = -V_1^2 \left(\frac{\partial p}{\partial V}\right)_S.$$

First quantity is proportional to tangent of angle of inclination of straight line BA, and the second quantity is proportional to tangent of angle of inclination of tangent line of shock adiabat H_B at point B (shock adiabat H_B and Poisson adiabat which passes through B are tangent to one another). Relative location of straight line BA and adiabat H_B corresponds to the case in which $u_1 < c_1$.

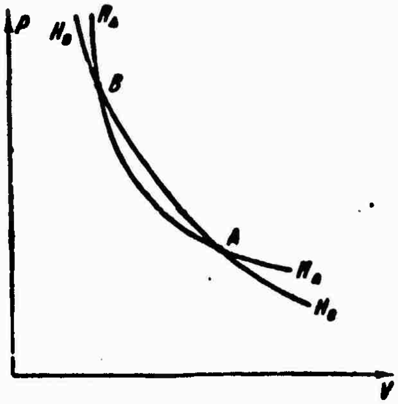

Fig. 1.30. p, V-diagram clarifying relationship between velocities of gas and sound in shock wave.

At the end of § 12 it was noted that, in distinction from Poisson adiabat, Hugoniot adiabat depends on two parameters. Because

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*The fact that adiabat H_B passes to the left of H_A at pressures higher than p_B can be explained in the following way: If point B corresponds to compression of gas from state A by a very strong shock wave, then adiabat H_A at $p > p_B$ goes almost vertically, corresponding to limiting compression to a volume equal to $[(\gamma - 1)/(\gamma + 1)]\,V_A$. At the same time, by passing a second shock wave through the gas from state B, we can compress it to the volume

$$[(\gamma-1)/(\gamma+1)]\,V_B = [(\gamma-1)/(\gamma+1)]^2\,V_A.$$

of this, it is impossible by means of compression of gas by several shock waves, proceeding from given initial state, to arrive at the very same final state as by means of compression by one wave.

Thus, for instance, if we pass a strong shock wave through a monatomic gas, the gas will be compressed by four times, but if we pass two strong waves through, one after the other, leaving final pressure unchanged, we will obtain compression by 16 times.

At the same time, by breaking up the adiabatic process into as many stages as desired, we will arrive at the same density, if final pressure is given.

This situation is illustrated by p, V-diagram of Fig. 1.31, where there are depicted Poisson adiabat and several Hugoniot adiabats, which correspond to compression of gas by successive shock waves.

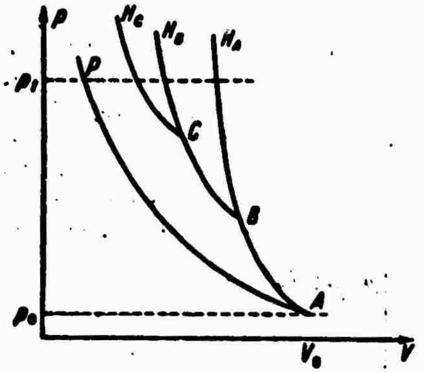

Fig. 1.31. Concerning the question of single and multiple shock and adiabatic compressions of gas to identical pressure p_1. H_A, H_B, H_C are shock adiabats for which points A, B, C are initial. P is Poisson adiabat.

§ 17. Impossibility of Existence of Rarefaction Shock Wave in Substance with Normal Properties

In § 13 there were written formulas for calculation of different quantities connected with a shock wave for the case of an ideal gas with constant heat capacity. From these formulas it directly followed that in a shock wave in which there occurs compression of substance, there are satisfied the following inequalities:

$$p_1 > p_0, \quad \varrho_1 > \varrho_0, \quad V_1 < V_0, \quad u_0 > c_0, \quad u_1 < c_1, \quad S_1 > S_0. \qquad (1.86)$$

Simultaneously with compression of substance and increase of its pressure, entropy increases; wave propagates through undisturbed gas with supersonic speed, but through compressed gas behind it with subsonic speed. This set of conditions is schematically depicted in Fig. 1.32a. We will now extend expressions (1.75) for shock adiabat to pressures lower than initial, and assume that there exist shocks in which there occurs not compression, but rarefaction of the gas: $V_1 > V_0$, $p_1 < p_0$. Laws of conservation of mass, momentum, and energy, with the help of which there were obtained formulas relating velocity, density, and pressure on both sides of the shock, in no way limit the possibility of existence of such shocks. From formulas (1.83) – (1.84) it is clear that in this case $u_0 < c_0$, a $u_1 > c_1$. Formula (1.85) for jump of entropy in the shock indicates that entropy of gas thus decreases (expression in braces is less than unity at $p_1 < p_0$).

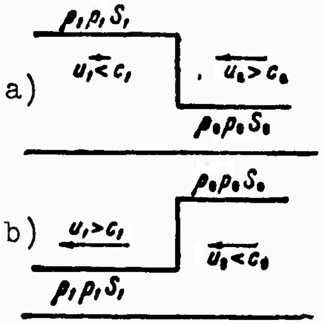

Fig. 1.32. Schematic representations of compressive shock waves (a) and rarefaction shock waves (b). Gas flows into shock from the right to the left.

We arrive, thus, to the regime of a rarefaction shock wave, in which there simultaneously are satisfied the following inequalities:

$$p_1 < p_0, \quad \rho_1 < \rho_0, \quad V_1 > V_0, \quad u_0 < c_0, \quad u_1 > c_1, \quad S_1 < S_0, \qquad (1.87)$$

and which schematically is depicted in Fig. 1.32b.

Geometric interpretation of these inequalities, which is similar to the one presented in § 16, is represented in Fig. 1.33. Slope of straight line AB is less than slope of tangent to shock adiabat H_A at point of initial state A ($u_0 < c_0$) and greater than slope of tangent to second shock adiabat H_B, which is drawn through point of final state

B $(u_1 > c_1)$.

Poisson adiabat P, which passes through point A in the region $p_1 < p_0$, drifts higher than shock adiabat H_A. This explains decrease of entropy during shock rarefaction. During adiabatic rarefaction to the same volume V_1, pressure p' is higher than final p_1. In order to come from Q to B, it is necessary to cool gas at constant volume, i.e., to decrease its entropy.

But, by the second law of thermodynamics, entropy of a substance cannot decrease due to only internal processes, without heat removal to the outside. From this follows the impossibility of propagation of a rarefaction wave in the form of a shock and of the two conditions whose existence is allowed by the laws of conservation of mass, momentum, and energy, the requirement of growth of entropy selects only one — the compressive shock wave. This statement has an absolutely general character and is known under the name of Cemplen theorem. In the following section it will be shown that in waves of weak intensity, under the condition of positivity of second derivative $(\partial^2 p/\partial V^2)_S > 0$, the sets of inequalities (1.86) or (1.87) are satisfied simultaneously, absolutely independently of specific thermodynamic properties of the substance. This theorem can also be proven for waves which are not of small amplitude and for an arbitrary substance. The only condition which is imposed on properties of substance is the condition that shock adiabat at all points is convex downwards: $(\partial^2 p/\partial V^2)_H > 0$, just as this occurs for an ideal gas with constant heat capacity. Overwhelming majority of real substances possess namely such properties, so that the statement about impossibility of existence of rarefaction shock waves has a very general character (below we will discuss certain exceptions).

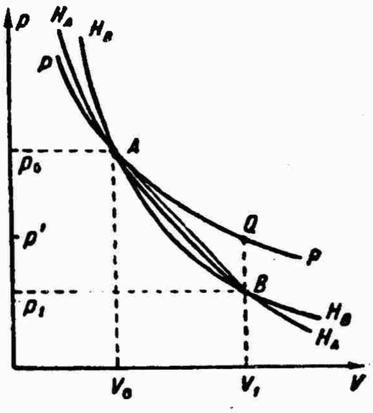

Fig. 1.33. Concerning geometric interpretation of inequalities in a "rarefaction shock wave." H_A is shock adiabat; P is Poisson adiabat passing through point A of initial state; H_B is shock adiabat drawn from point of final state B.

Impossibility of existence of rarefaction shock wave can be explained in the following way: Such a wave would propagate through undisturbed gas with subsonic speed $u_0 < c_0$. This means that if at some moment of time there appeared a state similar to the one depicted in Fig. 1.32b, then the perturbation from jump of density and pressure would travel to the right with speed of sound c_0, outstripping the "shock wave"; after a certain time, the rarefaction would involve the gas before the "shock" and the shock would simply be diffused. In other words, the rarefaction shock wave is mechanically unstable. Conversely, compressive shock wave propagates through undisturbed gas with supersonic speed $u_0 > c_0$; state behind this wave front in no way can influence state of gas before wave, and the shock remains stable. Relative to the compressed gas, compressive shock wave propagates with subsonic speed $u_1 < c_1$; therefore, gas-dynamic conditions behind shock front affects amplitude of wave.

If, let us say, we heat or compress gas behind the shock front, then the shock wave will be strengthened; and conversely, if behind the shock front there occurs cooling or rarefaction of the gas, then perturbations carrying the rarefaction overtake the shock wave and weaken it.

In a rarefaction shock wave, the situation would be the opposite: inasmuch as it would propagate through rarefied gas with supersonic speed, it would not be subject to the influence of any processes occurring behind it — it would be "uncontrolled."

It is very significant that the condition of mechanical stability of a shock wave coincides with the thermodynamic condition of increase of entropy. Mechanical stability can exist only if wave propagates through undisturbed substance with supersonic speed; otherwise, perturbation caused by the shock wave would penetrate into the initial gas with speed of sound, and would outstrip the shock wave, thereby diffusing the sharp front of the wave. At the same time, with the condition of increase of entropy there coincides a condition which allows us to imagine the causal relationship of phenomena. Namely, during increase of entropy, compressive shock wave propagates through the gas which has undergone transformation with subsonic speed, i.e., external factors such, for instance, as the piston thrust into the gas, can cause appearance of shock wave and subsequently influence its propagation.

Thus, in a substance with normal thermodynamic properties, when $(\partial^2 p/\partial V^2)_S > 0$, compressive shock waves, which correspond to increase of entropy, turn out to be mechanically stable and subject to the influence of external factors. Appearance of rarefaction shock wave is impossible from thermodynamic point of view, as well as from the point of view of stability: a once appearing steep rarefaction front would diffuse with flow of time.

Let us give in the conclusion of this section a table illustrating possibility of realization of different regimes:

	Compressional wave	Rarefaction wave
Shock	Possible; entropy increases; mechanical stability;	Impossible; entropy decreases; mechanical instability
Smooth distribution	Impossible; unlimited build-up of steepness of front, which becomes "overlapping"	Possible; distributions become with flow of time smoother and smoother

§ 18. Shock Waves of Weak Intensity

Let us consider a shock wave of weak intensity, in which jumps of all gas-dynamic parameters can be considered as small quantities. We will not for now make any assumptions about thermodynamic properties of the substance; we start only with laws of conservation.

Considering internal energy as a function of entropy and specific volume, we will write increment of energy in shock wave in the form of an expansion in small increments of independent variables near point of initial state:

$$\varepsilon_1-\varepsilon_0=\left(\frac{\partial\varepsilon}{\partial S}\right)_V(S_1-S_0)+\left(\frac{\partial\varepsilon}{\partial V}\right)_S(V_1-V_0)+\frac{1}{2}\left(\frac{\partial^2\varepsilon}{\partial V^2}\right)_S(V_1-V_0)^2+ \\ +\frac{1}{6}\left(\frac{\partial^3\varepsilon}{\partial V^3}\right)_S(V_1-V_0)^3.$$

All derivatives in this expansion are taken at point of initial state V_0S_0. As we now will see, increment of entropy in wave $S_1 - S_0$ is a quantity of third order of smallness, if we consider increment $V_1 - V_0$ as a small quantity of first order. Therefore, if we are limited to expansion of internal energy up to quantities of third order, we can omit terms which are proportional to $(S_1 - S_0)(V_1 - V_0)$, $(S_1 - S_0)^2$, etc. According to thermodynamic identity $d\varepsilon = T\,dS - p\,dV$,

$$\left(\frac{\partial\varepsilon}{\partial S}\right)_V=T,\quad \left(\frac{\partial\varepsilon}{\partial V}\right)_S=-p.$$

Therefore,

$$\varepsilon_1-\varepsilon_0=T_0(S_1-S_0)-p_0(V_1-V_0)-$$
$$-\frac{1}{2}\left(\frac{\partial p}{\partial V}\right)_S(V_1-V_0)^2-\frac{1}{6}\left(\frac{\partial^2 p}{\partial V^2}\right)_S(V_1-V_0)^3.$$

We will substitute this expression in equation of Hugoniot adiabat (1.71) and expand in its right side pressure p_1. Inasmuch as left side of equality can be expanded up to quantities of third order, in expansion of pressure it is sufficient to be limited to terms of the second order with respect to difference $V_1 - V_0$, and to omit the term containing increment of entropy, since it will give in the right side a term proportional to $(S_1 - S_0)(V_1 - V_0)$, which is a quantity of higher order of smallness than $(V_1 - V_0)^3$:

$$p_1=p_0+\left(\frac{\partial p}{\partial V}\right)_S(V_1-V_0)+\frac{1}{2}\left(\frac{\partial^2 p}{\partial V^2}\right)_S(V_1-V_0)^2.$$

After cancelling out in equation of Hugoniot adiabat with the substituted expansions, we will obtain the relation of increment of entropy to increment volume:

$$T_0(S_1-S_0)=\frac{1}{12}\left(\frac{\partial^2 p}{\partial V^2}\right)_S(V_0-V_1)^3. \qquad (1.88)$$

If we start with equation of Hugoniot adiabat written in form (1.72), where in place of internal energy there stands enthalpy, we will obtain in an analogous way

$$T_0(S_1-S_0)=\frac{1}{12}\left(\frac{\partial^2 V}{\partial p^2}\right)_S(p_1-p_0)^3. \qquad (1.89)$$

It is easy to verify the identity of both formulas by substituting expansion $(p_1 - p_0) = (\partial p/\partial V)_S (V_1 - V_0)$ into formula (1.89) and noticing that

$$\frac{\partial^2 V}{\partial p^2}=\frac{\partial}{\partial p}\frac{\partial V}{\partial p}=\frac{\partial}{\partial p}\left(\frac{1}{\partial p/\partial V}\right)=\frac{\partial}{\partial V}\left(\frac{1}{\partial p/\partial V}\right)\frac{1}{\partial p/\partial V}=-\left(\frac{\partial p}{\partial V}\right)^{-3}\left(\frac{\partial^2 p}{\partial V^2}\right).$$

Formulas (1.88) and (1.89) show that increment of entropy in shock wave of weak intensity is a quantity of third order of smallness with respect to increments $p_1 - p_0$ or $V_0 - V_1$, which characterize amplitude of wave.

From formulas (1.88) and (1.89) it is clear that sign of increment of entropy in shock wave is determined by signs of second derivatives $(\partial^2 p/\partial V^2)_S$ or $(\partial^2 V/\partial p^2)_S$. If adiabatic compressibility of substance $-(\partial V/\partial p)_S$ decreases with increase of pressure, i.e., $(\partial^2 V/\partial p^2)_S > 0$ and $(\partial^2 p/\partial V^2)_S > 0$, the usual adiabat on plane of p, V is depicted by a curve which is convex downwards (as in an ideal gas with constant heat capacity). In this case entropy increases $(S_1 > S_0)$ in compressive shock wave, when $p_1 > p_0$, $V_1 < V_0$, and decreases in rarefaction shock wave. If, however, $(\partial^2 V/\partial p^2)_S < 0$, $(\partial^2 p/\partial V^2)_S < 0$, the situation is reversed: entropy increases in the rarefaction shock wave, when $p_1 < p_0$, $V_1 > V_0$, and decreases in the compressive shock wave. Inasmuch as for the overwhelming majority of real substances $(\partial^2 V/\partial p^2)_S > 0$, then from condition of impossibility of decrease of entropy there follows the impossibility of existence of rarefaction shock waves. This theorem has already been formulated above and demonstrated in the concrete example of an ideal gas with constant heat capacity.

Let us write the expansion of pressure $p = p(S, V)$ near initial point S_0, V_0 up to terms of third order with respect to $V_1 - V_0$ and of first order with respect to $S_1 - S_0$:

$$p_1 - p_0 = \left(\frac{\partial p}{\partial V}\right)_S (V_1 - V_0) + \frac{1}{2}\left(\frac{\partial^2 p}{\partial V^2}\right)_S (V_1 - V_0)^2 + \\ + \frac{1}{6}\left(\frac{\partial^3 p}{\partial V^3}\right)_S (V_1 - V_0)^3 + \left(\frac{\partial p}{\partial S}\right)_V (S_1 - S_0).$$

We will describe by this expansion initial sections of the shock adiabat and usual adiabat which are drawn through point S_0, V_0. Terms of first and second orders of smallness with respect to $V_1 - V_0$ for both adiabats coincide, i.e., shock and usual adiabats have at initial point common tangents and common centers of curvature (there exists contact of the second order). Terms of third order of smallness differ for the adiabats. Third term in the right side of the expansion for both adiabats is common. The last term — the fourth — for usual adiabat vanishes, since $S_1 - S_0 = 0$ ($S = \text{const}$), and for the shock adiabat, according to (1.88), it is equal to

$$\left(\frac{\partial p}{\partial S}\right)_V (S_1 - S_0) = -\frac{1}{12T_0}\left(\frac{\partial p}{\partial S}\right)_V \left(\frac{\partial^2 p}{\partial V^2}\right)_S (V_1 - V_0)^3.$$

For all normal substances, pressure with increase of entropy at constant volume (during heating at constant volume) is increased, i.e., $(\partial p/\partial S)_V > 0$; $(\partial^2 p/\partial V^2)_S$ also is positive. Consequently, for $V_1 > V_0$, the last term is negative, and for $V_1 < V_0$ it is positive: for $V_1 > V_0$ the shock adiabat passes below the usual one, and for $V_1 < V_0$ it passes above the usual one. Thus, at the initial point for both adiabats there occurs contact of the second order with intersection.

Relative location of shock adiabat H and usual adiabat P is shown in Fig. 1.34. For clarity let us note that segment CD is a quantity of first order of smallness with respect to $V_0 - V_1$, DE is of second order, and EF is of third order.

Let us return to geometric interpretation of increase of entropy in shock wave (Fig. 1.35). As was shown in § 16, quantity $\bar{T}\Delta S$ is depicted by area of figure AFBCEA. Let us break it by a straight line AC into two parts: segment ACEA and triangle ABC. Area of triangle ABC is equal to half of product of base BC and height $V_0 - V_1$. Line segment BC during small changes of all quantities, i.e., in a wave of weak intensity, is equal to $\left(\frac{\partial p}{\partial S}\right)_V \Delta S$, i.e., to

$$\bar{T}\Delta S = F_{\text{cerm}} + \frac{1}{2}\left(\frac{\partial p}{\partial S}\right)_V (V_0 - V_1)\Delta S.$$

where F_{segm} is area of segment ACEA. Hence

$$\Delta S=\frac{F_{\text{сегм}}}{\overline{T}-\alpha},\alpha=\frac{1}{2}\left(\frac{\partial p}{\partial S}\right)_V(V_0-V_1).$$

For small changes of volume $\alpha \to 0$ and $\overline{T}\,\Delta S \to F_{segm}$, i.e., correction for area of triangle is small. And, indeed, it is of higher order of smallness than area of the segment, which has order of $\overline{T}\,\Delta S$. Forming expression for area of segment

$$\overline{T}\Delta S=\frac{p_0+p'}{2}(V_0-V_1)-\int_{V_1}^{V_0}(p\,dV)_{S=S_0}$$

and substituting expansions for weak waves, we will arrive, as we should have expected, at formula (1.88).

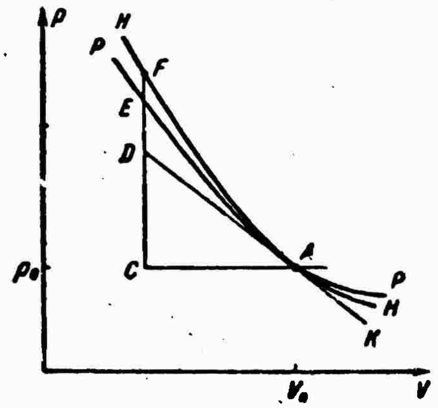

Fig. 1.34. Relative location of shock H and usual P adiabats. DK is tangent to adiabats at point of initial state A. In shock wave of weak intensity, line segment CD is a quantity of first order of smallness; DE is of second and EF is of third order of smallness.

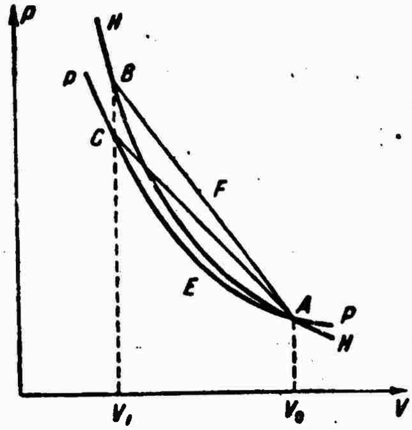

Fig. 1.35. Geometric interpretation of increment of entropy in shock wave.

Thus, from the geometric construction it is clear that sign of ΔS depends on sign of area of segment, i.e., on whether secant AC passes above or below usual adiabat, or, which is the same, whether adiabat is convex downwards or upwards.

Let us compare velocities u_0, u_1 with speeds of sound c_0, c_1. As we know, ratio u_0/c_0 is determined by ratio of slopes of straight line AB (see Fig. 1.28) and tangent to Poisson adiabat at point A. Ratio u_1/c_1 is determined by ratio of slopes of straight line AB and tangent to Poisson adiabat drawn through B. Let us write expressions for slopes of all three straight lines:

$\frac{p_1-p_0}{V_1-V_0}=\left(\frac{\partial p}{\partial V}\right)_{S_0}+\frac{1}{2}\left(\frac{\partial^2 p}{\partial V^2}\right)_{S_0}(V_1-V_0)$ → straight line AB;

$\left(\frac{\partial p}{\partial V}\right)_{S_A}=\left(\frac{\partial p}{\partial V}\right)_{S_0}$ — tangent to adiabat at point A;

$\left(\frac{\partial p}{\partial V}\right)_{S_B}=\left(\frac{\partial p}{\partial V}\right)_{S_0}+\left(\frac{\partial^2 p}{\partial V^2}\right)_{S_0}(V_1-V_0)$ — tangent to adiabat at point B.

The last formula follows from that fact that adiabat S_1 = const up to terms of third order with respect to $V_1 - V_0$ is parallel to adiabat S_0 = const. Noticing that

$$\left(\frac{\partial p}{\partial V}\right)_{S_0}<0, \left(\frac{\partial^2 p}{\partial V^2}\right)_{S_0}>0,\ V_1-V_0<0,$$

we see that straight line AB is steeper than tangent at point A, but not as steep as tangent at point B, whence $u_0 > c_0$, $u_1 < c_1$. This one may directly see from Fig. 1.30.

The inherent relation between conditions of increase of entropy and the condition of mechanical stability of a shock $u_0 > c_0$ is most important. Both conditions directly ensue from that fact that the adiabats with decrease of volume, starting from A, become steeper and steeper.

Thus, from consideration of shock waves of weak intensity in substance with arbitrary thermodynamic properties, we have obtained all those results from laws of conservation which were demonstrated above in the particular example of an ideal gas with constant heat capacity. The only condition which was required by us was positivity of second derivative $(\partial^2 p/\partial V^2)_S$.

§ 19. Shock Waves in Substance with Anomalous Thermodynamic Properties

Let us now imagine a substance with anomalous thermodynamic properties, such that second derivative $(\partial^2 p/\partial V^2)_S$ at least in a certain part of the adiabat is negative. Usual adiabat of such a substance in corresponding region of pressures and volumes is convex upwards, as shown in Fig. 1.36.

From consideration of preceding paragraph it follows that during small changes of pressure, the Hugoniot adiabat almost coincides with Poisson adiabat (with accuracy up to small terms of third order with respect to $V_1 - V_0$ or $p_1 - p_0$).

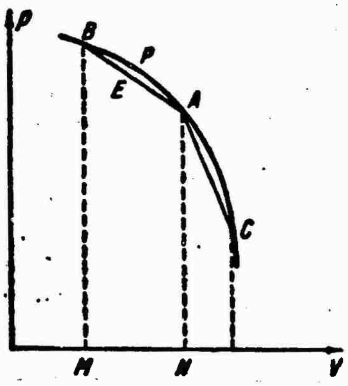

Fig. 1.36. Poisson adiabat of substance with anomalous properties and geometric interpretation of relationships for shock waves of compression and rarefaction.

In this case, area of figure APBMNA, which is bounded above by Poisson adiabat, is larger than area of trapezoid AEBMNA, which is bounded above by secant AEB, i.e., entropy in compressive shock wave decreases (this may be seen from formula (1.88)). At the same time, due to the fact that slope of secant is less than slope of tangent at point A, speed of propagation of shock wave through undisturbed gas is less than speed of sound, but inasmuch as slope of secant AEB is larger than slope of tangent at point B, speed behind shock is supersonic.

Conversely, in rarefaction shock wave entropy increases (see formula (1.88)). As can be seen from comparison of slopes of secant AC and tangents at points A and C, speed before shock is supersonic, and behind shock is subsonic.

Thus, even in a substance with anomalous properties, condition of increase of entropy coincides with condition of mechanical stability $u_0 > c_0$ and condition which allows causal relationship between external factors and propagation of wave: $u_1 < c_1$. In an anomalous substance compressive shock waves are impossible, but shock waves of rarefaction are possible. Compression caused by motion of piston in such a substance will propagate in the form of a wave, which gradually expands like rarefaction waves in a usual gas. Shock in general will not appear and motion will be adiabatic. Rarefaction wave will propagate in the form of a steep front, which will not expand with flow of time, and thickness of which will be determined by values of viscosity and thermal conductivity.

Under usual conditions, all substances — gaseous, solid, and liquid — possess normal properties: their adiabatic compressibility decreases with increase of pressure.

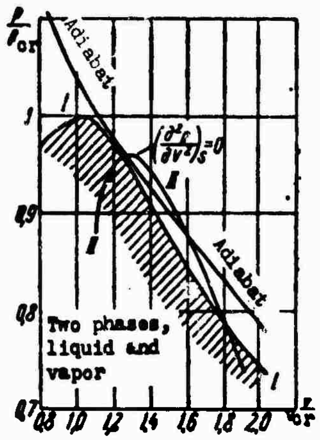

Fig. 1.37. Adiabat with anomalous convexity in Vander Waals gas with heat capacity $c_V = 40$ cal/deg·mole. Shaded region of two-phase systems. Curve II bounds region of states with anomalous convexity of adiabats. Under curve II $(\partial^2 p/\partial v^2)_S < 0$.

Anomalous behavior of a substance may be expected near the liquid—gas critical point. Actually, still long before the critical point is reached, isotherms of gas have an inflection (at the critical point, the inflection becomes horizontal). For a substance with sufficiently high molecular heat capacity, for which adiabatic index is close to unity, adiabats and isotherms little differ, and it is possible to expect that outside of the region of two-phase states adiabats also will have an inflection, i.e., will have a region with anomalous sign of second derivative, as this is shown in Fig. 1.37, taken from book of Ya. B. Zel'dovich [2].

Curve I on this figure bounds region of two-phase system, and curve II is locus of points of inflection of adiabats $(\partial^2 p/\partial V^2)_S = 0$. It separates region in which $(\partial^2 p/\partial V^2)_S < 0$. In Fig. 1.37 there is drawn also one adiabat possessing anomaly. Curves are calculated with help of model equation of state of Vander Waals for case of heat capacity $c_V = 40$ cal/deg·mole.

The connection between sign of increase of entropy and inequalities concerning speeds of gas and sound, which correspond to obligatory coincidence of condition of growth of entropy with condition of mechanical stability, can be disturbed only in the case when in the considered interval of change of pressure there are realized both signs of $\partial^2 p/\partial V^2$, so that Poisson adiabat has more than two points of intersection with the secant. Thus there can appear complicated regimes with simultaneous existence of both shocks and diffuse waves adjacent to them.

One more case of anomalous behavior of a substance will be considered in Chapter XI; anomalies in this case are connected with polymorphous transformations (phase transitions) of solid bodies at those high pressures which are attained in shock waves. In the same place there will be considered also the indicated complicated regimes.

3. Viscosity and Thermal Conduction in Gas Dynamics

§ 20. Equations of One-Dimensional Motion of Gas

Dissipative processes — viscosity (internal friction) and thermal conduction — are connected with existence of molecular structure of substance. They create additional, non-hydrodynamic transfer of momentum and energy and lead to non-adiabatic character of motion and to thermodynamically irreversible transformation of mechanical energy into heat. Viscosity and thermal conduction appear only in the presence of large gradients of hydrodynamic quantities, which occur, for instance, in boundary layer during flow around bodies or inside the shock front. In this book viscosity and thermal conduction will interest us basically from the point of view of their influence on internal structure of shock fronts in gases. During the study of this structure, flow can be considered to depend on one coordinate x (plane), since thickness of front of shock wave always is considerably less than radius of curvature of its surface. Therefore, we will not dwell on derivation of general equation of motion of a viscous liquid (gas), which can be found, for instance, in book of L. D. Landau and E. M. Lifshits [1], but will explain only how there can be obtained equation for one-dimensional, plane case.

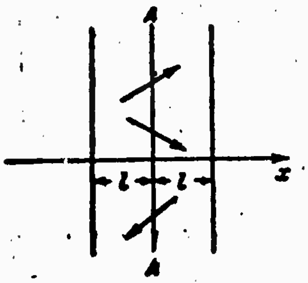

Fig. 1.38. Diagram explaining derivation of formula for molecular transfer of momentum.

We will write equation of conservation of momentum for an inviscid gas (1.7) in the plane case, when all quantities depend only on one coordinate x, and velocity has only one x-th component of u

$$\frac{\partial}{\partial t}(\rho u) = -\frac{\partial \Pi_{xx}}{\partial x}, \quad \Pi_{xx} = p + \rho u^2.$$

We will take into account now the fact that gas consists of molecules colliding with each other. Let us imagine an element of unit cross section perpendicular to axis x. This element from both sides is pierced by molecules flying in definite directions after they have experienced their last collisions.

Molecules emerge after last collision from layers of thickness of the order of mean free path of molecules l, which border the element on both sides (Fig. 1.38). If n is number of molecules in 1 cm^3, and $\bar{v}$ is their average thermal velocity, then in 1 sec the element is intersected from the left to the right by on the order of $n\bar{v}$ molecules. Each of them transfers through the element hydrodynamic momentum mu, where m is mass of a molecule, i.e., flux density of hydrodynamic momentum from the left to the right in order of magnitude is equal to $n\bar{v} \cdot mu$. Analogously, flux of hydrodynamic momentum from the right to the left is equal approximately to $n\bar{v}m\ (u + \Delta u)$, where Δu is increment of hydrodynamic velocity during transition from left layer to right: $\Delta u \approx \frac{\partial u}{\partial x} l$. Flux density of x-th component of momentum in x-direction connected with molecular transfer is equal to difference between fluxes from the left to the right and from the right to the left, i.e., $-\ n\bar{v}ml\ \frac{\partial u}{\partial x}$. This quantity corresponds to additional transfer of momentum due to internal friction; it must be added to momentum flux density $\Pi_{xx} = p + \rho u^2$.

More rigorous treatment, based on study of three-dimensional motion, shows that into the written expression there should be introduced a numerical coefficient of the order of unity. Namely, equation of conservation of momentum, taking into account viscosity, in the plane case has the form

$$\frac{\partial}{\partial t}(\rho u) = -\frac{\partial \Pi_{xx}}{\partial x}, \quad \Pi_{xx} = p + \rho u^2 - \sigma', \quad \sigma' = \frac{4}{3}\eta\frac{\partial u}{\partial x}, \tag{1.90}$$

where η is coefficient of viscosity, which for gases (in the absence of relaxation processes; see below) in order of magnitude is equal to

$$\eta \sim n\bar{v}ml = \rho\bar{v}l.$$

Quantity σ' constitutes the xx-component of tensor of viscous stresses. Appearance of it in formula for flux of momentum is equivalent to appearance of additional "pressure", which is due to forces of internal friction. From equation (1.90), with help of continuity equation, it is easy to go over to equation of motion

$$\rho\frac{du}{dt}=-\frac{\partial}{\partial x}(p-\sigma'). \tag{1.91}$$

$\frac{\partial\sigma'}{\partial x}$ is force of internal friction calculated for 1 cm^3 of gas.

In the presence of dissipative processes, additional terms also appear in energy equation. With additional, "viscous" pressure there is connected additional energy flow. To the expression of energy current density, which stands under the sign of divergence in formula (1.10), it is necessary to add the quantity $-\sigma' u$, which is analogous to pu. Furthermore, into this expression there should be introduced flow of energy which is transferred by mechanism of thermal conduction:

$$J=-\varkappa\frac{\partial T}{\partial x}, \tag{1.92}$$

where $\varkappa$ is coefficient of thermal conductivity. Expression (1.92) is easy to obtain by the same means by which there was found viscous flux of momentum. Thus it turns out that in gases, the coefficient of thermal conductivity in order of magnitude is equal to $\varkappa \sim \rho c_p \bar{v} l$.

Taking into account both dissipative terms, energy equation (1.10), written for the plane case, acquires the form

$$\frac{\partial}{\partial t}\left(\rho\varepsilon+\frac{\rho u^2}{2}\right)=-\frac{\partial}{\partial x}\left[\rho u\left(\varepsilon+\frac{u^2}{2}\right)+pu-\sigma' u+J\right]. \tag{1.93}$$

By transforming this equation with help of continuity equation, equation of motion and thermodynamic identify $T\,dS = d\varepsilon + p\,dV$, we will obtain equation for rate of change of entropy of a particle of the substance:

$$\rho T\frac{dS}{dt}=\sigma'\frac{\partial u}{\partial x}-\frac{\partial J}{\partial x}=\frac{4}{3}\eta\left(\frac{\partial u}{\partial x}\right)^2+\frac{\partial}{\partial x}\left(\varkappa\frac{\partial T}{\partial x}\right). \tag{1.94}$$

First term in the right side of this equation constitutes mechanical energy dissipated in 1 cm^3 in 1 sec due to viscosity. It is always positive, since $\eta > 0$ and $(\partial u/\partial x)^2 > 0$; consequently, forces of internal friction lead to local increase of entropy of substance. Second term corresponds to heating or cooling of substance due to thermal conduction. It can be positive, as well as negative, since thermal conduction leads to transfer of heat from hotter regions into cooler ones. However, entropy of all of the substance on the whole due to thermal conduction only increases. Of this we can be convinced if we divide equation (1.94) by T and integrate over the entire volume. Change of entropy of substance occupying volume bounded by surfaces x_1 and x_2 due to thermal conduction is equal to

$$\int_{x_1}^{x_2} \frac{1}{T}\frac{\partial}{\partial x}\left(\varkappa\frac{\partial T}{\partial x}\right)dx = \frac{1}{T}\varkappa\frac{\partial T}{\partial x}\Big|_{x_1}^{x_2} + \int_{x_1}^{x_2}\frac{\varkappa}{T^2}\left(\frac{\partial T}{\partial x}\right)^2 dx.$$

If substance is thermally insulated on boundaries x_1 and x_2, then fluxes of heat on boundaries disappear and there remains only second term in the right side, which is always positive ($\varkappa > 0$).

Equations of gas dynamics, written taking into account viscosity and thermal conduction, permit us to determine under what conditions the role of these dissipative processes can become important.

Let us compare inertial forces in equation of motion with viscosity forces. If U is scale of velocity, and d are characteristic dimensions of region involved in motion, then scale of time is of the order of d/U, and inertial term $\rho\, du/dt$ is of the order of $\rho U^2/d$. Viscosity term in equation $\frac{\partial}{\partial x}\left(\frac{4}{3}\eta\frac{\partial u}{\partial x}\right)$ is of the order of $\eta U/d^2$ and the ratio of it to the inertial term is of the order of

$$\frac{1}{\mathrm{Re}} = \frac{\eta}{\rho U d} = \frac{\nu}{Ud} \sim \frac{l}{d}\frac{c}{U};$$

Reciprocal of this ratio has the name Reynolds number ($\nu = \eta/\varrho \sim l\bar{v} \sim lc$ is kinematic viscosity, $c \sim \bar{v}$ is speed of sound). In an analogous way, by comparing heat transfer by means of thermal conduction with mechanical transfer of energy, we will find that their ratio is of the order of

$$\frac{1}{\mathrm{Pe}} = \frac{\varkappa}{\varrho c_p U d} \sim \frac{\chi}{U d} \sim \frac{l}{d} \frac{c}{U},$$

where Pe is Peclet number, which is close in gases to Reynolds number, since coefficient of molecular thermal diffusivity $\chi = \varkappa/\rho c_p$ is close to coefficient of kinematic viscosity ν. (For instance, in air under normal conditions $\nu \approx \chi \approx 0.15$ cm^2/sec).

Thus, viscosity and thermal conduction can be disregarded at $\mathrm{Re} \approx \mathrm{Pe} \gg 1$. If we consider motion with velocities less than or equal to speed of sound, dimensions of system for this have to be much larger than mean free path of molecules $d/l \gg 1$. This condition, as we will see, is not satisfied, in particular, in region of shock wave front, thickness of which is comparable with mean free path of molecules. Therefore, inside shock wave front, dissipative processes turn out to be essential. Namely they lead to increase of entropy in the shock wave.

§ 21. Remarks about Second Viscosity

During writing of equations of gas dynamics and use of thermodynamic relation between pressure and other thermodynamic characteristics of substances, it was tacitly assumed that pressure p, which determines forces in the moving gas, does not differ from static pressure p_{stat} measured in gas at rest under the same conditions (i.e., with the same composition of gas, density of gas, internal energy, temperature). Pressure is a scalar quantity which does not depend on selection of system of coordinates, on directions of velocity, and gradient of velocity. Requirement of scalar character of pressure, of its invariance with respect to transformations of coordinates, allows an assumption which is more general than the assumption about dependence only on thermodynamic state of the substance. Pressure, in general, can depend on a scalar — the divergence of velocity. For small gradients, if we limit ourselves to first terms of the expansion, as in the derivation of viscous forces, we can write the general expression

$$p = p_{\text{cт}} + \xi \operatorname{div} \mathbf{u}, \tag{1.95}$$

where coefficient ξ characterizes dependence of forces acting in the substance on the scalar div **u**. Coefficient ξ is called second viscosity. In distinction from it, coefficient η, the first viscosity, characterizes forces depending on directions of velocity and its gradient. Coefficient of first viscosity in gas is connected with translational thermal motion of molecules. If time of establishment of static pressure is of the order of mean free time of molecules l/c, ξ has the same order as η. In the plane case, both terms with first and second viscosity thus are joined together. In certain cases, however, ξ has anomalously large value. According to continuity equation $\operatorname{div} \mathbf{u} = -\frac{1}{\rho}\frac{d\rho}{dt}$, i.e., coefficient ξ characterizes dependence of pressure on rate of change of density.

In the presence of internal, slowly excited degrees of freedom in a substance (for instance, vibrations in molecules) and fast changes of state of substance, pressure does not have time to "follow" change of density, and differs from a thermodynamically equilibrium quantity. Influence of this effect can be described with help of coefficient of second viscosity (see [1]), where the more difficult it is to excite internal degrees of freedom, the greater the "mismatching" of changes of pressure and changes of density and internal state of substance, and the greater the second viscosity. In very fast processes, when this "mismatching" (deviation from thermodynamic equilibrium) is especially great, linear dependence (1.95) may be insufficient, and into the equations of gas dynamics it is necessary to introduce in explicit form a description of relaxation processes — kinetics of excitation of internal degrees of freedom. We will meet with this phenomenon in Chapters VI, VII, VIII during consideration of relaxation processes, their influence on structure of fronts of shock waves and absorption of ultrasound.

§ 22. Remarks about Sound Absorption

As an example of the influence of viscosity and thermal conduction on hydrodynamic motion, we will consider process of propagation of sound waves, taking into account these phenomena.

Presence of viscosity and thermal conduction leads to dissipation of energy of sound waves, to irreversible transformation of it into heat, i.e., to absorption of sound and decrease of its intensity. Formally the coefficient of sound absorption can be obtained if we seek the solution of one-dimensional linearized equations of gas dynamics, taking into account viscosity and thermal conduction, in the form of a plane harmonic wave of type $\exp[i(kx - \omega t)]$, where k is wave vector. Thus for k there is obtained a complex value, the real part of which gives wave length, and the imaginary part of which gives coefficient of absorption: $k = k_1 + ik_2$; $\exp[i(kx - \omega t)] = e^{-k_2 x} e^{i(k_1 x - \omega t)}$. Coefficient of absorption can be estimated also from physical considerations. According to formula (1.94), energy dissipated in 1 cm^3 in 1 sec is composed of two parts, which correspond to viscosity and thermal conduction. In a sound wave with wave length λ, these quantities are of the order of $\eta u^2/\lambda^2$ and $\varkappa \Delta T/\lambda^2$. Here u is the amplitude of velocity, and ΔT is amplitude of change of temperature in wave (the latter is proportional to u). Energy of sound in 1 cm^3 is $\rho_0 u^2$. Fraction of energy which is absorbed in 1 sec consists of two terms. The term connected with viscosity is of the order of $(\eta u^2/\lambda^2)/\varrho_0 u^2 \sim \eta/\varrho_0\lambda^2 \sim \eta\omega^2/c^2\varrho_0$. But in 1 sec sound traverses distance c, so that coefficient of absorption per unit of length is of the order of $\gamma_1 \sim \eta\omega^2/c^3\rho_0$. Coefficient of absorption per unit of length which is connected with thermal conduction is of the order of $\gamma_2 \sim \frac{\varkappa}{c_p}\frac{\omega^2}{c^3\varrho_0}$ (in case of gases this is easy to understand if we consider that $\varkappa/c_p \approx \eta$ in virtue of approximate equality of kinematic viscosity $\nu = \eta/\rho$ and thermal diffusivity $\chi = \varkappa/\rho c_p$; in gases $\gamma_1 \approx \gamma_2$). These expressions are valid for small sound absorption, when decrease of amplitude at distances of the order of the wave length is small, i.e., $\gamma\lambda \ll 1$ $(\gamma = \gamma_1 + \gamma_2)$. In gases this condition means that

$$\gamma\lambda \sim \frac{\eta\omega^2\lambda}{c^3\varrho_0} \sim \frac{\nu}{\lambda^2}\frac{\lambda}{c} \sim \frac{l}{\lambda}\frac{\bar{v}}{c} \sim \frac{l}{\lambda} \ll 1,$$

i.e., expression for coefficient of absorption is valid for wave lengths considerably larger than mean free path of molecules, which actually always is the case.

In a substance with delayed excitation of internal degrees of freedom (with large second viscosity) there appear additional, anomalously large absorption, and also dispersion of sound (dependency of speed of sound on frequency). This problem will be considered in Chapter VIII.

§ 23. Structure and Width of Front of Shock Wave of Weak Intensity

Let us consider what are the internal structure and thickness of that thin layer in a shock wave in which there occurs transition of gas from initial state to final state and which is called the front of the shock wave. In this layer there occur sharp compression of substance, change of its pressure, velocity and, as calculations showed, based only on application of laws of conservation of mass, momentum, and energy, there occurs increase of entropy. The latter indicates that in transition layer there occurs dissipation of mechanical energy, irreversible transformation of it into heat. Therefore, in order to understand how shock compression occurs, it is necessary to take into consideration dissipative processes — viscosity and thermal conduction.

Let us consider plane one-dimensional flow of a viscous and heat-conducting gas in system of coordinates in which front of shock wave is at rest. Width of front is very small as compared to characteristic scales of length for all of the gas-dynamic process on the whole, for instance, as compared to distance from front of shock wave to piston pushing the gas and creating the wave.

Even if piston moves with variable speed and amplitude of shock wave changes in time, for that small time Δt in which front passes over distance of the order of its own width Δx, amplitude of wave remains practically constant. Therefore, for the period of a certain time, which is small as compared to total time scale of gas-dynamic process, but large in comparison with Δt, the whole pattern of distribution of gas-dynamic quantities in the wave front propagates through the gas in "frozen" form as a whole. In other words, in a system of coordinates in which the front is at rest, flow of gas can at every given moment be considered to be steady.

Let us write equations of continuity, momentum, and entropy, taking into account viscosity and thermal conduction for the plane steady case. Inasmuch as process is steady-state, partial derivative with respect to time ∂/∂t can be omitted, and partial derivative with respect to coordinate ∂/∂x can be replaced by total derivative d/dx:

$$\frac{d}{dx}(\varrho u)=0,$$
$$\frac{d}{dx}\left(p+\varrho u^2-\frac{4}{3}\eta\frac{du}{dx}\right)=0,$$
$$\varrho uT\frac{dS}{dx}=\frac{4}{3}\eta\left(\frac{du}{dx}\right)^2+\frac{d}{dx}\left(\varkappa\frac{dT}{dx}\right). \qquad (1.96)$$

With help of second law of thermodynamics $T\,dS = dw - V\,dp$ and equations of continuity and momentum, entropy equation can be written in form of energy equations:

$$\frac{d}{dx}\left[\varrho u\left(w+\frac{u^2}{2}\right)-\frac{4}{3}\eta u\frac{du}{dx}-\varkappa\frac{dT}{dx}\right]=0. \qquad (1.97)$$

We will subject solution of these equations to boundary conditions, according to which gradients of all quantities before the front, at $x = -\infty$, and after the front, at $x = +\infty$ vanish, and the actual quantities take their initial and final values, to which we as before will assign indices "0" and "1" (Fig. 1.39).

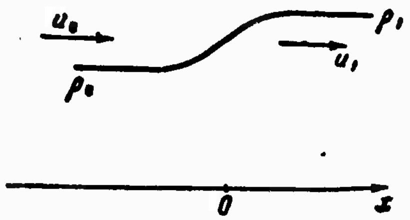

Fig. 1.39. Diagram illustrating formulation of problem about structure of front of shock wave.

First integrals of system of equations of mass, momentum and energy are obtained immediately:

$$\varrho u=\varrho_0u_0, \qquad (1.98)$$
$$p+\varrho u^2-\frac{4}{3}\eta\frac{du}{dx}=p_0+\varrho_0u_0^2, \qquad (1.99)$$
$$\varrho u\left(w+\frac{u^2}{2}\right)-\frac{4}{3}\eta u\frac{du}{dx}-\varkappa\frac{dT}{dx}=\varrho_0u_0\left(w_0+\frac{u_0^2}{2}\right). \qquad (1.100)$$

Constants of integration here are expressed in terms of initial values of quantities p, ρ, T, u and are considered as functions of current coordinate x.*

From equation (1.99) it is clear that due to presence of viscosity, i.e., term containing du/dx, distribution of quantities over x in wave front should be continuous (otherwise gradient du/dx would go to infinity, which is incompatible with finiteness of the quantities themselves).

For the purpose of best understanding of roles of each of the processes, viscosity and thermal conduction, we will first consider two particular cases of structure of front: 1) when there is no viscosity and there exists one thermal conduction; 2) when there exists one only viscosity, but there is no thermal conduction. We will here not look for exact solutions of equations (this problem will be considered in Chapter VII, which is specially dedicated to study of structure of shock wave fronts). Let us limit ourselves only to clarifying qualitative picture of phenomenon and estimates of width of front.

1) <u>Thermal conduction exists, but there is no viscosity</u> $\eta = 0$.

This case is remarkable due to the fact that equation of momentum (1.99) acquires the form

$$p+\rho u^2=p_0+\rho_0 u_0^2,$$

which is analogous to that form which connects final and initial values of quantities. However now this equation describes all intermediate states in wave front. With help of continuity equation

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*At $x = +\infty$ du/dx = 0, dT/dx = 0, $p = p_1$, $\rho = \rho_1$, $u = u_1$, and we arrive at laws of conservation of mass, momentum, and energy on the shock (1.61), (1.62), (1.64).

(1.98), we will obtain

$$p = p_0 + \rho_0 u_0^2 \left(1 - \frac{V}{V_0}\right). \tag{1.101}$$

Thus, the point describing state of gas inside shock wave front travels on p, V-plane from initial point A to final point B along straight line AB, about which we already have said much during investigation of shock adiabat.

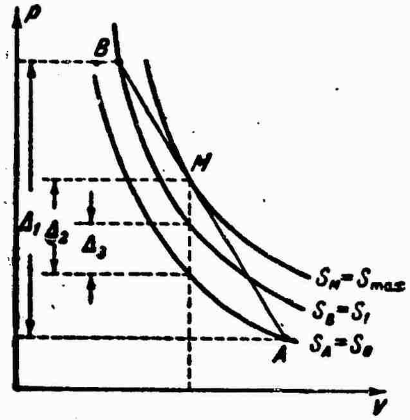

Fig. 1.40. p, V-diagram pertaining to problem about structure of shock wave front without taking into account viscosity. State in wave changes along straight line AB. Segments Δ_1, Δ_2, Δ_3 are of first, second and third orders of smallness with respect to amplitude of wave.

We will draw through points of initial and final states on p, V-plane Poisson adiabats (Fig. 1.40; Hugoniot adiabat is not shown on it). If we plot on the plane a whole series of Poisson adiabats with various values of entropy, then we will see that one of them is tangent to straight line AB at a certain point M, as shown in Fig. 1.40. At this point entropy along straight line AB is maximum ($S_0 < S_1 < S_M$). From equations (1.98) and (1.101) it follows that velocity of gas u at point of tangency M is exactly equal to local speed of sound (u = c at point M; we recall that at point A $u_0 > c_0$, and at point B $u_1 < c_1$).

Let us find magnitude of maximum of entropy S_{max} from condition of tangency of Poisson adiabat with $S = S_{max}$ and straight line AB. As we will now see, quantity $S_{max} - S_0$ is proportional to $(V_1 - V_0)^2$ or $(p_1 - p_0)^2$; therefore, equations of family of adiabats p (V, S) and straight line we will write in the form of expansion near point A, omitting terms of third order of smallness (in such an approximation adiabats S_0 and S_1 coincide; see § 18). Equation of adiabat has the form:

$$p-p_0=\left(\frac{\partial p}{\partial V}\right)_{S_A}(V-V_0)+\frac{1}{2}\left(\frac{\partial^2 p}{\partial V^2}\right)_{S_A}(V-V_0)^2+\left(\frac{\partial p}{\partial S}\right)_{V_A}(S-S_0).$$

Equation of straight line:

$$p-p_0=\frac{p_1-p_0}{V_1-V_0}(V-V_0)=\left(\frac{\partial p}{\partial V}\right)_{S_A}(V-V_0)+\frac{1}{2}\left(\frac{\partial^2 p}{\partial V^2}\right)_{S_A}(V_1-V_0)(V-V_0).$$

Condition of tangency is expressed by equality $\left(\frac{\partial p}{\partial V}\right)_{\text{adiab}} = \left(\frac{\partial p}{\partial V}\right)_{\text{str}}$, which gives equation for determination of volume V_M at point of tangency M.

Calculation shows that point M is found exactly in the middle between points A and B: $V_M - V_0 = \frac{1}{2}(V_1 - V_0)$. Substituting this expression into equation of straight line, we will find pressure at point M, and substituting then the found value of pressure p_M and volume V_M into equation of adiabat and solving it for entropy, we will obtain entropy at point M:

$$S_M-S_0=S_{\max}-S_0=\frac{1}{8}\frac{(\partial^2 p/\partial V^2)_{S_A}}{(\partial p/\partial S)_{V_A}}(V_1-V_0)^2.$$

Thus, maximum change of entropy inside front of shock wave during consideration of only thermal conduction is a magnitude of the second order of smallness with respect to amplitude $V_0 - V_1$ or $p_1 - p_0$, in distinction from total jump of entropy $S_1 - S_0$, which is of the third order of smallness with respect to amplitude. This is clear from geometric considerations: the greatest distance of straight line AB from Poisson adiabat $S = S_0$ on p, V-plane is proportional to $(V_1 - V_0)^2$ or $(p_1 - p_0)^2$. Thus, the difference between pressures at point M and on adiabat S_A (or S_B) at the very same volume V_M is equal to

$$p_M(V_M)-p_{S_A}(V_M)=\frac{1}{2}\left(\frac{\partial^2 p}{\partial V^2}\right)_{S_A}\times(V_M-V_0)(V_1-V_M)=\frac{1}{8}\left(\frac{\partial^2 p}{\partial V^2}\right)_{S_A}(V_1-V_0)^2 \quad (1.102)$$

(difference of pressures between points on adiabats S_B and S_A at identical volume V_M is a magnitude of third order of smallness).

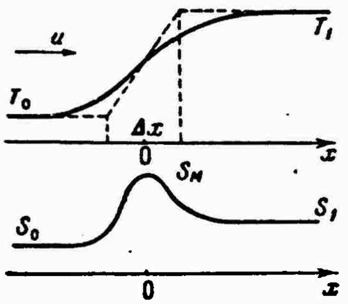

Fig. 1.41. Distributions of temperature and entropy in weak shock wave front without taking into account viscosity. Δx — effective width of front.

Presence of maximum of entropy inside the front indicates that profile of temperature T (x) at point where entropy is maximum has an inflection, so that distributions of temperature and entropy in a weak shock wave with only thermal conduction are depicted by curves shown in Fig. 1.41. This follows from entropy equation (1.97), which in absence of viscosity takes the form

$$\rho u T \frac{dS}{dx} = \frac{d}{dx} \varkappa \frac{dT}{dx} = \varkappa \frac{d^2T}{dx^2} \qquad (1.103)$$

(in a weak wave the temperature changes little, so that coefficient of thermal conductivity can be considered to be constant). Existence of maximum of entropy is connected with the fact that thermal conduction transfers heat from region with higher temperature to region with lower temperature. Therefore, the gas flowing in a wave at first is heated due to thermal conduction (with increase of entropy), and then is cooled (with decrease of entropy). In the end, as compared to initial value, entropy of course increases. This is illustrated by Fig. 1.41: advance along axis x with velocity u (x) corresponds to following the change of state of a given particle of gas with time.

Let us now estimate width of wave front. For this we will divide equation (1.103) by T and will integrate it over x from initial state A ($x = -\infty$), where $dT/dx = 0$, to some point x in the wave (thus we will use the fact that $\rho u = \rho_0 u_0 = \text{const}$):

$$\rho_0 u_0 (S - S_0) = \varkappa \int_{-\infty}^{x} \frac{1}{T} \frac{d^2T}{dx^2} dx = \varkappa \left\{ \frac{1}{T} \frac{dT}{dx} + \int_{T_0}^{T} \frac{dT}{dx} \frac{1}{T^2} dT \right\}. \qquad (1.104)$$

We will apply this equation to point of final state B ($x = +\infty$), where $dT/dx = 0$.

Thus the first term in brackets vanishes and

$$\varrho_0 u_0 (S_1 - S_0) = \varkappa \int_{T_0}^{T_1} \frac{1}{T^2} \frac{dT}{dx} \, dT.$$

We will determine effective width of shock wave front Δx, in the presence only of thermal conduction, by equality

$$\frac{T_1 - T_0}{\Delta x} = \left| \frac{dT}{dx} \right|_{\max},$$

the geometric meaning of which is clear from Fig. 1.41.

Considering for estimate of the integral that $dT/dx \sim (T_1 - T_0)\Delta x$, we will find

$$\varrho_0 u_0 (S_1 - S_0) \sim \varkappa \frac{1}{T_1^2} \frac{(T_1 - T_0)^2}{\Delta x}.$$

Expressing temperature jump in terms of pressure jump, we will obtain:

$$T_1 - T_0 = \left(\frac{\partial T}{\partial p} \right)_S (p_1 - p_0) = \frac{V_0}{c_p} (p_1 - p_0),$$

where c_p is heat capacity at constant pressure; using formula (1.89) for jump of entropy, and considering approximate equalities for gases $\left(\frac{\partial^2 V}{\partial p^2} \right)_S \sim \frac{V_0}{p_0^2}$, $\varkappa \sim \varrho_0 c_p l c_0$, and also the fact that $u_0 \approx c_0$, we will obtain from (1.104) an estimate of width of front:

$$\Delta x \sim l \frac{p_0}{p_1 - p_0}. \qquad (1.105)$$

Width of front is inversely proportional to amplitude of wave, where as its scale there serves mean free path of molecules l.

From equation (1.104) it is also possible to estimate magnitude of maximum increase of entropy. At point of maximum of entropy $dS/dx = 0$, gradient dT/dx is maximum. Thus, the main role in braces (1.104) is played by first term, which is proportional to $\Delta T/\Delta x \sim \Delta p/\Delta x \sim (\Delta p)^2$, while second term is proportional to $(\Delta T)^2/\Delta x \sim (\Delta p)^3$. Hence it is clear that $S_{\max} - S_0 \sim (\Delta p)^2$, while $S_1 - S_0 \sim (\Delta p)^3$.

Considering internal structure of shock wave front, and taking into account only thermal conduction, it is possible to say only that temperature in wave changes continuously. Other quantities — density, velocity, pressure — in general can undergo a discontinuity. And indeed, consideration of structure of shock waves without taking into account viscosity shows that at sufficiently large amplitude it is impossible to construct a continuous distribution for all quantities in the wave. This difficulty was noted by Rayleigh (detail about this see in § 3, Chapter VII). It indicates the fundamental role of viscosity in realization of irreversible shock compression of substance in a wave.

Let us consider now the second particular case.

2) Viscosity exists, but there is no thermal conduction: $\varkappa = 0$.

Then it is necessary to retain the general equation of momentum (1.99). On p, V-plane the point describing state in wave travels the path from point A to point B no longer along straight line AB, but along a certain curve, which is depicted in Fig. 1.42 by a dotted line.

From the entropy equation without the thermal conduction term

$$\varrho u T \frac{dS}{dx} = \eta \left(\frac{du}{dx}\right)^2 \qquad (1.106)$$

it follows that entropy in wave monotonically increases from initial value $S_0 = S_A$ to final value $S_1 = S_B$, so that dotted line is wholly contained between Poisson adiabats S_0 and S_1 (see Fig. 1.42).

Inasmuch as adiabats are convex downwards $((\partial^2 p/\partial V^2)_S > 0$, dotted line lies wholly below straight line AB).*

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*Really, vertical distance between adiabats S_1 and S_0 is proportional to $S_1 - S_0 \sim (p_1 - p_0)^3$, while vertical distance between points A and B is $p_1 - p_0$. Therefore, section of straight line AN on which dotted line in principle could pass above straight line is a quantity which is small as compared to the main part of straight line NA.

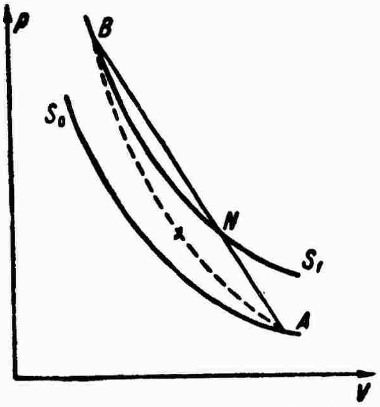

Fig. 1.42. p, V-diagram pertaining to problem about structure of shock wave front without taking into account thermal conduction. State in wave changes along dotted curve AB.

Equation of curve along which there occurs transition from point A to point B is

$$p = p_0 + \varrho_0 u_0^2 \left(1 - \frac{V}{V_0}\right) + \frac{4}{3}\eta \frac{du}{dx}. \quad (1.107)$$

Inasmuch as curve lies wholly below the straight line, at all points inside wave $du/dx < 0$. If x-axis is directed in the direction of motion of gas, then $u > 0$, i.e., gas in wave only is retarded, and consequently is monotonically compressed. Thus, consideration of structure of shock wave front, taking into account viscosity, leads to the case in which for $(\partial^2 p/\partial V^2)_S > 0$ there is possible only compression of gas in shock wave. Profiles of velocity and density in wave have the form depicted in Fig. 1.43.

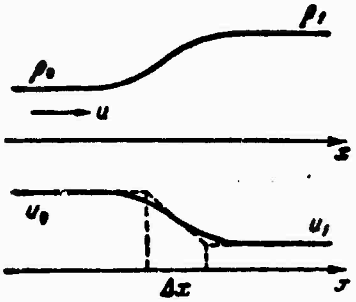

Fig. 1.43. Profiles of density and velocity in shock wave front: Δx is effective width of wave.

We will determine effective width of front Δx by equality

$$\frac{u_0 - u_1}{\Delta x} = \left|\frac{du}{dx}\right|_{\max}, ^* \quad (1.108)$$

analogously to the preceding. Geometric meaning of it is clear.

Maximum absolute value of gradient $|du/dx|_{\max}$ is determined according to (1.107) by maximum vertical deviation

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*Δx is called sometimes Prandtl width of front.

of straight line AB from dotted line, i.e., from Poisson adiabats S_0 or S_1. This deviation, as we already know, corresponds to middle of segment AB and is given by formula (1.102). Thus,

$$\frac{4}{3}\eta\left|\frac{du}{dx}\right|_{\max} \approx \frac{1}{8}\left(\frac{\partial^2 p}{\partial V^2}\right)_{S_A}(V_1-V_0)^2.$$

Substituting this expression for $\left| du/dx \right|_{\max}$ in (1.108), and noticing that $\eta = \rho_0\nu \sim \rho_0 l\bar{v} \sim \rho_0 l c_0$ (ν is kinematic viscosity), and also that

$$u_0-u_1=\sqrt{(p_1-p_0)(V_0-V_1)}\sim\sqrt{(p_1-p_0)^2\left|\frac{\partial V}{\partial p}\right|}\sim\frac{p_1-p_0}{p_0}c_0,\quad\left(\frac{\partial^2 p}{\partial V^2}\right)_S\sim\frac{p_0}{V_0^2},$$

we will arrive at formula (1.105) for width of front:

$$\Delta x\sim l\frac{V_0}{V_0-V_1}\approx l\frac{p_0}{p_1-p_0}.$$

Width of front can be estimated also with help of entropy equation (1.106) analogously to the way this was done in the first case:

$$\varrho_0 u_0 T_0\frac{S_1-S_0}{\Delta x}\sim\eta\frac{(u_0-u_1)^2}{\Delta x^2}.$$

Substituting here expression (1.89) for jump of entropy and making simple transformations, we will arrive at former formula for Δx.

During construction of continuous solution with only viscosity, no difficulties similar to those which appear during consideration of only thermal conduction appear. This circumstance, as already was noted, has a deep physical basis and testifies to the fundamental role of viscosity in realization of shock compression. Namely, viscosity is the mechanism due to which there occurs irreversible transformation of part of kinetic energy of flow incident on shock into heat, i.e., transformation of energy of directed motion of molecules of gas into energy of random motion due to scattering of their momentum.

Thermal conduction in this sense plays an indirect role, since it leads only to transfer of energy of random motion of molecules from one place to another, but does not influence the directed motion directly.

If we consider shock waves of not too great amplitude in an ordinary gas, in which transport coefficients — kinematic viscosity ν and thermal diffusivity χ — are approximately identical and are determined by the same mean free path of molecules $l(\nu \approx \chi \sim lc)$, then we as before will obtain formula (1.105) for width of front. This is easy to check by considering general entropy equation (1.98), taking into account viscosity as well as thermal conduction.

Formula (1.105) shows that for a pressure jump in the wave of the order of magnitude of the actual pressure before the front, width of front is of the order of the mean free path of molecules. With further increase of amplitude of wave, if we use the same formula, width becomes less than mean free path. This result, of course, does not have physical meaning. If gas-dynamic quantities strongly change at distances of the order of mean free path of molecules, then hydrodynamic consideration of viscosity and thermal conduction, at basis of which lies the assumption about smallness of gradients, loses validity.

Width of an arbitrarily strong shock wave of course cannot become less than mean free path of molecules, which is indicated by consideration, based on use of kinetic equation for gas (see Chapter VII).

Under certain conditions there is possible considerable broadening of front of strong shock waves to distances equal to many lengths of mean free path, and separation of it into regions of smooth and sharp change of quantities is possible. In particular, this occurs in a gas with delayed excitation of certain degrees of freedom of molecules or during the course of reversible chemical reaction in the wave. These problems, just as a whole series of others appearing during more detailed study of internal structure of shock wave fronts, will be considered in detail in Chapter VII.

4. Certain Problems

§ 24. Propagation of an Arbitrary Shock

Gas-dynamic quantities on each side of a shock wave front are not independent. They are related by definite relationships which express laws of conservation of mass, momentum, and energy. Thus a shock, a compressive shock wave in substances with normal thermodynamic properties, propagates through the substance as a stable formation, without spreading out.

Meanwhile there is possible a formulation of the problem in which at the initial moment in the gas there exists a discontinuity surface, on both sides of which gas-dynamic quantities in no way are related with each other — are absolutely arbitary. Such shocks are called arbitrary shocks.

Let us give several practical examples which show how arbitrary shocks arise. Let us imagine a pipe divided by a thin partition (barrier). Pipe is filled with gas, where densities and pressures and, in general, types of gas on right side of partition and on left side are different. Let us assume that at a certain moment the partition is rapidly removed. At this instant in the place where the partition was the two regions come into contact — two gases at rest with absolutely arbitrarily given densities and pressures. If pressures in each gas are different, then after removal of the partition the gases under action of the pressure drop will be set in motion. Second example. Let us assume that through a pipe filled with gas, from both ends there are sent shock waves with arbitrarily given amplitudes. At the time of collision of both waves somewhere in the middle of the pipe, there appears a surface dividing the gases with arbitrary pressures, velocities, and temperatures (possible differences in densities in this example are somewhat limited; we will say that if both waves are very strong, then densities in them are identical and equal to limiting density). After collision of waves, motion of gas will be changed in some way. Third example. We have approached the theory of shock waves considering the motion of a gas under action of a piston starting to be thrust into the gas with constant velocity. In this case the shock wave will be formed directly at the piston, at the initial moment and will propagate through the gas with constant velocity. In reality, of course, the piston, which has finite mass, cannot instantly acquire terminal velocity, but gathers it, gradually being accelerated under the action of force applied to it. Thus the shock wave will not be formed at once, and will be formed far from the piston.

It is possible to replace smooth law of change of velocity of piston in time U (t) by some step curve, by dividing time into very small intervals and assuming that in every such interval of time the velocity of piston is constant, and upon the expiration of this interval changes with a jump by a small amount. Then the curve of motion of the piston on x, t-plane will be depicted by a broken curve consisting of small line segments. In every small time interval, during the period of which velocity of piston is constant, piston sends forward a perturbation — a wave of compression, i.e., a weak shock wave. This wave travels through the gas with velocity slightly exceeding the speed of sound, whereas the preceding weak shock wave, which was caused by the preceding jump of velocity of piston, propagates relative to gas moving behind it with a velocity slightly less than speed of sound, as is shown in Fig. 1.44. Therefore, every successive shock wave catches up with the preceding wave, and the compressions carried by them are superimposed. If we draw on the x, t-plane characteristics going out from curve of motion of piston, then they will intersect (Fig. 1.45). It turns out that it is possible to assign a law of acceleration to the piston such that all of these weak shock waves overtake one another at one moment and at one point. Then all of the numerous little pulses of compression are accumulated into one large jump. (All characteristics intersect at one point).

State of gas in this shock changes from undisturbed to final almost adiabatically. Indeed, if all of the compression of initial gas to pressure p is divided into n stages, n weak shock waves with jump of pressure $\Delta p = (p - p_0)/n$, then in each of them the increase of entropy ΔS is proportional to $(\Delta p)^3 \sim {}^1/n^3$, and total increase of entropy with cumulation of n waves is proportional to $n\Delta S \sim 1/n^2 \to 0$ as $n \to \infty$. Thus, states of gas on each side of shock appearing as a result of cumulation are related by Poisson adiabat. Meanwhile, in the shock wave, states on both sides of the shock are related with each other not by Poisson adiabat, but by Hugoniot adiabat.

Consequently, quantities on both sides of shock do not satisfy laws of conservation and the shock is arbitrary.

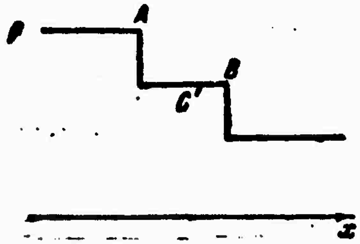

Fig. 1.44. Profile of pressure in system of two small compressive shocks following one after the other. Wave A travels through gas located in front of it with velocity higher than speed of sound c' in this gas. Wave B travels through gas located behind it with subsonic velocity, less than c'. Therefore, shock A finally overtakes shock B.

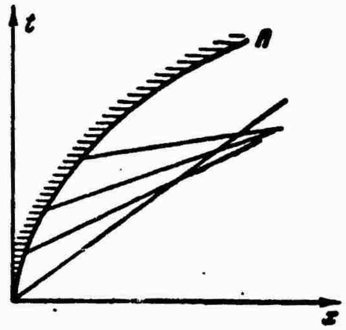

Fig. 1.45. Intersection of characteristics during compression of gas by accelerating piston. Π is line of piston.

By generalizing cases represented by the given examples, we will formulate idealized problem about finding motion of gas in which there appeared an arbitrary shock. Let us assume that at initial moment t = 0 in plane x = 0 all quantities undergo a discontinuity: pressure, density, velocity, temperature. On both sides of the shock all these quantities are constant. Types of gases on both sides also can differ. The larger the distance from discontinuity surface, on which parameters of gas can still be considered to be constant, the longer in time the solution to which we will arrive will be accurate (this problem was for the first time solved by N. Ye. Kochin [3]).

Inasmuch as in the conditions of the problem there are not contained characteristic lengths and times, we look for motion depending only on the ratio x/t. In § 11 it was shown that self-similar plane flow of gas can be described by solutions of only two types: there are possible centered simple rarefaction waves and motion in which all gas-dynamic quantities are constant. Furthermore, there can occur discontinuities — shock waves.

Thus, the unknown motion should be constructed from three elements: rarefaction waves, regions of constant flow, and shock waves. The set of possible motions is limited by the fact that in one direction there cannot move more than one wave (it makes no difference which kind — rarefaction or shock).

Shock wave propagates through undisturbed gas with supersonic speed, but through compressed gas in it — with subsonic speed. Rarefaction wave travels through gas with speed of sound. If, for instance, through gas to the right there travels a shock wave, then rarefaction wave following after it in the same direction, and all the more so a shock wave, will necessarily overtake it in a certain time. But in virtue of self-similarity, both waves emerge from one point $x = 0$ at the same moment $t = 0$. Therefore, one wave as it were already has overtaken the other at the very initial moment, and both of them propagate in the form of one. In exactly the same way, it is impossible for a second wave to follow behind the rarefaction wave. Shock wave would overtake rarefaction wave, and second rarefaction wave would move behind the first at a fixed distance, which in virtue of self-similarity is equal to zero, so that difference between both waves disappears.

Thus, the unknown solution can be constructed only in the form of some combination of two waves, shock waves and rarefaction waves, which propagate in opposite directions from initial shock and are separated by regions of constant flow. There are in general two of these regions. They are differentiated by a plane dividing those gases which at the inital moment were located on each side of the arbitrary shock. Inasmuch as in hydrodynamics of an ideal fluid, diffusion of molecules is not taken into account, interpenetration of gases into each other is lacking, and boundary between them will be retained, in some way moving in space together with the gases. The case when gases are of one type obviously does not represent a fundamental difference (we will imagine that molecules of gas on one side of initial shock are "colored"). This plane boundary between the two gases, which can be called the contact boundary or contact discontinuity possesses specific properties. Obviously, pressures and velocities of gases on both sides of contact discontinuity coincide with each other. Otherwise near it there would appear motion and regions of gas on both sides would cease to be regions of constant flow. Densities, temperatures, and entropies of gases on each side of contact discontinuity can remain arbitrary, in accordance with the arbitrariness in initial values. Difference between these quantities during equality of pressures and velocities in no way can set gases in relative motion (of course, under the assumption of absence of diffusion and thermal conduction, to the influence of which we will return somewhat later).

Contact discontinuity is at rest relative to gases and does not send perturbations which could influence waves (shock and rarefaction) travelling in both directions from it.

We will enumerate possible motions of gas after appearance of arbitrary shock: so to speak, cases of disintegration of shock, which constitute different combinations of rarefaction and shock waves. There can be presented three typical cases: 1) in both directions from shock there are propagated shock waves; 2) in one direction travels a shock wave, but in the other — a rarefaction wave; and

3) in both directions there travel rarefaction waves.

Let us examine these cases more specifically. For this, it is convenient to use p, V-diagram (Fig. 1.46). First of all we will fix on the diagram initial states of gases. Point A presents gas on the left of the shock, point B — on the right. Let us assume for definiteness that pressure at point $A(P_a)$ is less than P_b. Let us draw upwards from these points Hugoniot adiabats describing compression of gases in shock waves, and downwards — Poisson adiabats, along which there occurs expansion of gases in rarefaction waves. After disintegration of shock, pressures in both gases in regions subjected to influence of waves are equalized.

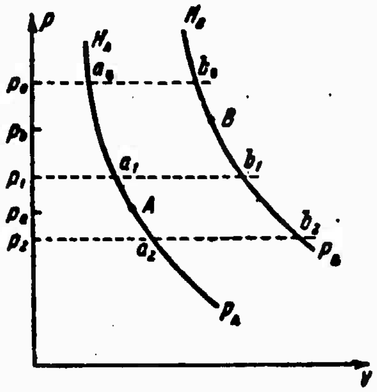

Fig. 1.46. p, V-diagram illustrating different cases of disintegration of arbitrary shock. Points A and B describe initial states of gases A and B. H_AA and H_BB are shock adiabats, AP_A, BP_B are Poisson adiabats of gases A and B.

1. Let us assume that this new pressure p_0 is higher than initial p_a and p_b.

In this (first) case both to the right and to the left from arbitrary shock (or from contact surface) there travel compressive shock waves (Fig. 1.47a). Gases after them are in states a_0 and b_0 with identical pressures p_0 and velocities. Gas in state a_0 moves relative to initial gas in state A to the left and gas b_0 moves relative to gas B to the right. Inasmuch as gases a_0 and b_0 move with identical velocity, it is necessary that gases A and B at initial moment move toward each other. Two shock waves are formed during collision of the two gases moving toward each other with great velocity (we recall the second example). The less the velocity of collision, the lower the obtained pressure p_0 in the shock waves.

2. At some low velocity of collision, there appears a new regime, in which pressure p_1 is still higher than pressure p_a, but less than p_b. In this (second) case, through gas A after disintegration of shock there propagates a shock wave, and through gas B — a rarefaction wave (Fig. 1.47b). In particular, such a regime is realized when initial velocities of both gases, A and B, are identical and are equal to zero, i.e., when at initial moment in gases at rest there is a discontinuity of pressure, as in the example with the partition. Substance starts to move in the direction of pressure drop. This case has important practical applications. On this principle is based the mechanism of a shock tube, in which there are obtained in the laboratory strong shock waves, which heat the investigated gas A to high temperature. Shock tube is divided by a thin partition (diaphragm). On one side of the diaphragm in the tube there is contained investigated gas A at low pressure; on the other, into the so-called high pressure chamber there is pumped the working gas B. After burst of the diaphragm, gas B is expanded in the direction of the low pressure chamber, sending into gas A a strong shock wave. The appearing regime, which is depicted in Fig. 1.47b, will be more specifically considered in Chapter IV during the study of operation of shock tube. By appropriate selection of gases A and B and pressure drop, it is attempted to obtain as strong a shock wave as possible and heating of investigated gas to very high temperatures. One of methods of obtaining still higher temperatures is realization of first regime — collision of two shock waves. A particular case of the first regime is reflection of shock wave from end of shock

tube, which is also used for achievement in laboratory of high temperatures. Reflection of shock wave from hard wall indeed constitutes a particular case of collision of two gas flows. If two absolutely identical flows collide with one another, then after the collision the contact discontinuity is at rest, i.e., the situation is the same as if instead of a contact discontinuity there were a motionless hard wall. Problems of collision of shock waves and reflection of them from a wall also will be considered in Chapter IV.

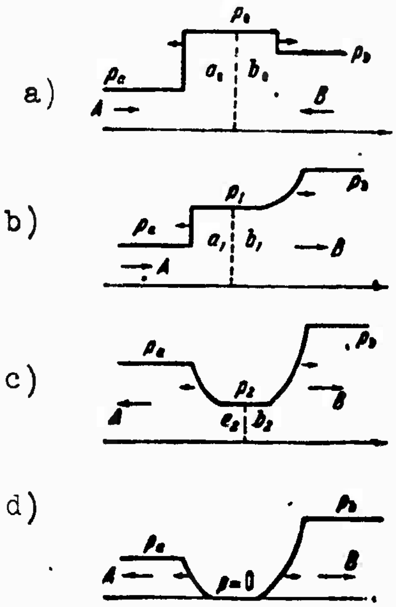

Fig. 1.47. Profiles of pressure in different cases of disintegration of a shock. Large arrows with letters A and B indicate initial velocities of gases A and B before disintegration of shock. Little arrows show direction of propagation of waves through mass of gas (direction of propagation in space can be in certain cases different).

3. If after disintegration pressure p_2 is less than p_a and p_b, we will obtain two rarefaction waves travelling to the right and to the left through both gases. This regime, which is depicted in Fig. 1.47c, is realized if at initial moment gases A and B move in opposite direction from shock with sufficiently high speed.

If relative velocity with which at initial moment gases A and B move away from each other is very great, namely, larger than sum of maximum velocities of flow of gases A and B into a vacuum, $\frac{2c_a}{\gamma_a - 1} + \frac{2c_b}{\gamma_b - 1}$, where c_a and c_b are initial speeds of sound and γ_a and γ_b are adiabatic indices of gases A and B (see § 11. formula (1.60)), then between gases there will be formed a vacuum, $p = 0$. This regime, which it is possible to consider as limit of the third case, is depicted in Fig. 1.47d.

During concrete calculations connected with disintegrations of arbitrary shocks, along with p, V-diagrams, very convenient are the so-called p, u-diagrams, on which along axes are plotted pressures p and velocities of gases u in laboratory system of coordinates. Shock adiabat of gas $p_H(V)$ can be represented in the form of a dependence of pressure behind wave front on jump of velocity of gas, i.e., on velocity of compressed gas relative to undisturbed gas. Likewise, in rarefaction wave pressure is uniquely connected with velocity by the condition of constancy of the Riemann invariant (see § § 10, 11). Convenience of p, u-diagrams in problem about disintegration of shock is connected with the fact that in final state pressures and velocities of both gases are identical, i.e., final states are depicted by the same point on the p, u-diagrams.

p, u-diagrams for cases of disintegration depicted in Fig. 1.47a-d are shown in Fig. 1.48a-d respectively.

After clarifying character of motions appearing during disintegration of an arbitrary shock, it is possible to check the initial assumption about the fact that motion depends only on the combination x/t. During examining of rarefaction wave in § 11, this assumption was supported by the fact that with passage of time, width of rarefaction wave, which is scale of length in the problem without consideration of dissipative processes, increases as $x \sim ct$. Role of viscosity and thermal conduction, which is proportional to l/x, with passage of time decreases, and in macroscopic flows, when $x \gg l$, is insignificantly small. Consequently the only constant scale of dimension of length in gas — mean free path of molecules — disappears.

During flows with shock waves, viscosity and thermal conduction, which introduce into the equation scale of length l, in reality act only in thin layer of wave front, width of which is of the order of l. Small also is the width of the contact shock. Broadening of it occurs due to processes of diffusion of molecules and thermal conduction. Both processes lead to width of shock of the order of $\Delta x \sim \sqrt{\chi t} \sim \sqrt{Dt}$, where D is coefficient of diffusion, which is close to coefficient of thermal diffusivity $D \sim \chi \sim lc$. Distance passed over by shock and rarefaction waves during the time t is of the order of $x \sim ct$, so that $\Delta x \sim \sqrt{lx}$. Thus, ratio of dimensions of region in which dissipative forces act to dimensions of the whole region involved in motion for a shock wave is of the order of l/x, and for contact shock $\sim\sqrt{l/x}$. Both quantities are small in macroscopic flow with $x \gg l$. Let us return to the third example given in beginning of this section, and see what regime appears during disintegration of shock which is formed as a result of cumulation of compressional waves sent by the accelerated piston. At the moment of joining of separate waves, on one side of the shock we will have undisturbed gas A, and on the other – gas in state B, which is subjected to practically adiabatic compression. It is possible to show that velocity which gas acquires during successive compression by a large number of shock waves is less than velocity acquired during single shock compression to the same pressure. It follows from this that the shock disintegrates as in case 2). Through the compressed gas to the piston will go a rarefaction wave, and through undisturbed gas – a shock wave. Pressure p will be lower than pressure created on piston p_b. However, due to increase of entropy in shock wave, this lower pressure corresponds to higher temperature, so that gas in shock wave will be heated comparably to the almost adiabatic heating due to cumulation of weak waves. In Fig. 1.49 there are represented distributions of p and T after disintegration of shock formed as a result of cumulation of waves during compression of air by a piston, whose speed gradually reached 4.44 c_0 = 1500 m/sec, so that pressure on piston reached $p_b = 50p_a = 50$ atm. Coordinate and time on figure are measured from point and moment of cumulation.

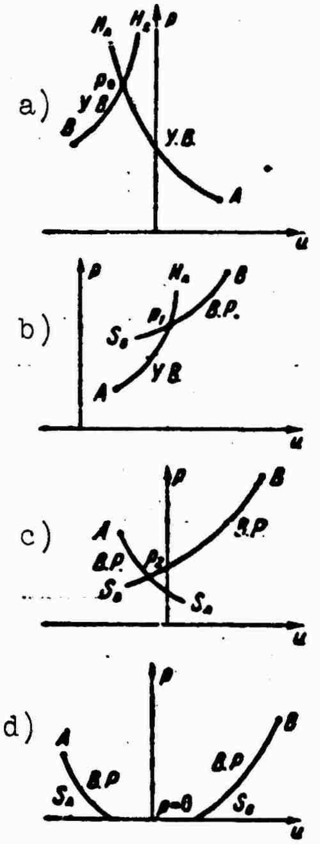

Fig. 1.48. p, u-diagram for different cases of disintegration of shock which are depicted in Fig. 1.47. Curves H are shock adiabats in variables p, u; curves S are Poisson adiabats in variables p, u; S.W. designates shock wave; R.W. designates rarefaction wave.

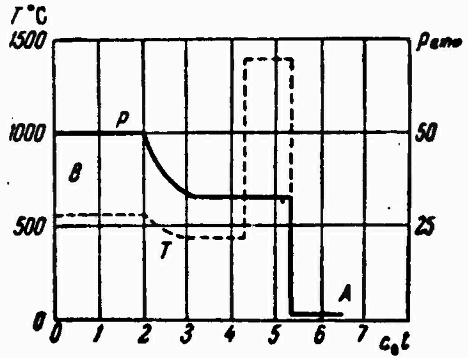

Fig. 1.49. Propagation of a shock which appears after collision of a set of consecutive compressional waves. Temperature in the appearing shock wave is considerably higher than maximum temperature attained during superposition of small compressional waves, but pressures are lower, since toward the compressional waves there travels a rarefaction wave. Profile of pressure is shown by solid line, profile of temperature — by dotted line.

The considered case presents considerable interest for theory of occurrence of detonation, since the obtained result explains how a flame acting on a gas like piston can by gradual compression cause appearance of a shock wave at a large distance from the flame (piston). By gradually compressing gas to fairly high temperature (630° C on the figure), it is possible to realize sharp heating to 1450° C at a considerable distance at the moment of cumulation, to realize "remote ignition." Apparently, such is the mechanism of appearance of detonation in gases in a number of cases.

§ 25. Strong Explosion in a Homogeneous Atmosphere

Idealized problem about a strong explosion in homogeneous atmosphere constitutes typical example of class of motions of gas called self-similar, when gas-dynamic quantities change with flow of time in such a way that distributions of them over coordinate remain always similar to themselves.

Self-similar problem about strong explosion was formulated and solved by L. I. Sedov. With a clever method, by means of use of integral of energy, L. I. Sedov succeeded in finding exact analytic solution of equations of self-similar motion [4, 5]. The problem was considered also by K. P. Stanyukovich (in dissertation; see [15]) and Taylor [6], who formulated and investigated the equations, but did not obtain their analytic solution.

We will dwell on formulation and results of solution of this problem, since they will be needed by us subsequently, in Chapters VIII and IX, during the study of certain physicochemical and optical phenomena accompanying strong explosion in air.

Let us assume that in gas of density ρ_0, which we will consider to be ideal, with constant heat capacity, in a small volume during short interval of time there is released high energy E. From place of energy release through the gas there propagates a shock wave. We will consider that stage of the process when the shock wave departs to distances which are very large as compared to dimensions of region where energy release occurred, and when motion involves a mass of gas which is large as compared to mass of products of the explosion. Thus energy release can with great accuracy be considered as occurring at a point, and instantaneously.

At the same time we will consider that this stage of the process is not too late, so that the shock wave departs from its source not too far, and its amplitude is still so high that it is possible to disregard initial pressure of gas p_0 as compared to pressure in shock wave. This is equivalent to the possibility of disregarding initial internal energy of gas involved in motion as compared to energy of explosion E, and of disregarding initial speed of sound c_0 in comparison with velocities of gas and wave front.

Motion of gas is determined by two dimensional parameters: energy of explosion E and initial density ρ_0. From these parameters it is impossible to compose scales with dimensions of length or time. Consequently, motion will be self-similar, i.e., will depend only on a definite combination of coordinate r (distance from center of explosion) and time t. In distinction from self-similar motion considered in § 11, in this problem there is no characteristic velocity. Initial speed of sound c_0 cannot characterize the process: in that same approximation in which initial pressure p_0 is assumed equal to zero, speed of sound c_0 is also equal to zero.* Therefore,

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*This condition actually determines bounds of applicability of solution of the problem. After presenting definite requirements for accuracy of the solution, we compare obtained pressures in wave front p_1 and velocity of propagation of wave D with real values of $p_0 c_0$ and find the moment when the approximation of $p_1 \gg p_0$ becomes too course. It is necessary to note that in fact the condition of validity of disregarding of initial pressure is somewhat more rigid, namely: $p_1 \gg [(\gamma + 1)/(\gamma - 1)]\, p_0$. This one may see from formula (1.76): under this condition compression in shock wave is equal to limiting value $(\gamma + 1)/(\gamma - 1)$.

self-similar variable is not the quantity r/t, as in self-similar rarefaction wave (see § 11).

The only dimensional combination containing length and time in this case is E/ρ_0: $[E/\rho_0] = [\mathrm{cm}^5\mathrm{sec}^{-2}]$. Therefore, as self-similar variable serves the dimensionless quantity:

$$\xi = r\left(\frac{\rho_0}{Et^2}\right)^{\frac{1}{5}}. \qquad (1.109)$$

To front of shock wave there corresponds a definite value of independent variable ξ_0; law of motion of front of wave R(t) is described by formula

$$R = \xi_0\left(\frac{E}{\rho_0}\right)^{\frac{1}{5}} t^{\frac{2}{5}}. \qquad (1.110)$$

Velocity of propagation of shock wave is equal to:

$$D = \frac{dR}{dt} = \frac{2}{5}\frac{R}{t} = \xi_0 \frac{2}{5}\left(\frac{E}{\rho_0}\right)^{\frac{1}{5}} t^{-\frac{3}{5}} = \frac{2}{5}\xi_0^{\frac{5}{2}}\left(\frac{E}{\rho_0}\right)^{\frac{1}{2}} R^{-\frac{3}{2}}.$$

Parameters of front are expressed in terms of velocity of front, with help of limiting formulas for strong shock wave:

$$\rho_1 = \rho_0\frac{\gamma+1}{\gamma-1}, \quad p_1 = \frac{2}{\gamma+1}\rho_0 D^2, \quad u_1 = \frac{2}{\gamma+1}D. \qquad (1.111)$$

Density on front remains constant and equal to its limiting value. Pressure decreases with flow of time according to the law

$$p_1 \sim \rho_0 D^2 \sim \rho_0\left(\frac{E}{\rho_0}\right)^{\frac{2}{5}} t^{-\frac{6}{5}} \sim \frac{E}{R^3}. \qquad (1.112)$$

It is easy to understand the physical meaning of laws of propagation of a strong blast wave. By moment t the wave attains radius R, and encompasses volume of gas $4\pi R^3/3$ and mass $M = \rho_0 \cdot 4\pi R^3/3$. Pressure is proportional to average energy of unit of volume, i.e., $p \sim E/R^3$. Velocities of front and gas are proportional to $D \sim u \sim \sqrt{p/\rho} \sim \sqrt{E/\rho_0 R^3}$. By integrating equation $dR/dt = D$, we will find dependence of radius of front on time, $R \sim (E/\rho_0)^{1/5} t^{2/5}$ (with accuracy up to numerical coefficient ξ_0).

Formula (1.112) demonstrates law of similarity for transition from certain energies of explosion to others. Pressure on front has given value at distances proportional to $E^{1/3}$, or at moments of time, proportional to $E^{1/3}$.

Distributions of pressure, density, and velocity of gas over the radius are determined by dependence on one dimensionless variable ξ, which can be represented in the form $\xi = \xi_0 r/R$. Shape of distributions, in virtue of self-similarity, does not change with flow of time; scales of quantities p, ρ, u depend on time in exactly the same way as values of these quantities on shock wave front. In other words, solution can be represented in the form

$$p=p_1(t)\tilde{p}(\xi), \quad u=u_1(t)\tilde{u}(\xi), \quad \rho=\rho_1\tilde{\rho}(\xi),$$

where $p_1(t)$, $u_1(t)$, p_1 are pressure, velocity, and density on shock wave front, which depend on time by known laws described by formulas (1.111) and (1.112), and $\tilde{p}(\xi)$, $\tilde{u}(\xi)$, $\tilde{\rho}(\xi)$ are new, dimensionless functions.

Substituting these expressions in equations of gas dynamics written for spherically-symmetric case, and going from differentiation with respect to r and t to differentiation with respect to ξ with help of relationship (1.109), just as this was done in § 11, we will obtain system of three ordinary first order differential equations in three unknown functions $\tilde{p}$, $\tilde{u}$, $\tilde{\rho}$. Solution of this system should satisfy conditions on wave front: for $\xi = \xi_0$, $\tilde{p} = \tilde{u} = \tilde{\rho} = 1$.

We will not expound here procedure of solution or write out final formulas, which can be found in books of L. I. Sedov [5] and L. D. Landau and E. M. Lifshits [1]. Let us note only that dimensionless parameter contained in solution ξ_0 is determined from condition of conservation of energy:

$$E=\int_0^R 4\pi r^2\rho\,dr\left(\varepsilon+\frac{u^2}{2}\right). \qquad (1.113)$$

if we substitute in it the found solution. It depends, just as the entire solution, on adiabatic index γ.

In real air adiabatic index is not constant; it depends on temperature and density due to processes of dissociation and ionization occurring at high temperature (see Chapter III). However, it is almost always possible to select a certain effective value of the index, considering it to be constant, in order to describe a real process by solution of idealized problem about strong explosion. For air it is possible to take values of γ equal approximately to 1.2-1.3.

In Fig. 1.50 there are depicted distributions of ratios p/p_1, ρ/ρ_1, u/u_1, T/T_1 over relative coordinate r/R for $\gamma = 1.23$; parameter ξ_0 thus is equal to $\xi_0 = 0.930$.

It is characteristic that during strong explosion, density of gas extraordinarily sharply falls from front of shock wave to center. Practically entire mass of gas, which earlier uniformly filled sphere of radius R, now is gathered in a thin layer near surface of front. Pressure near front decreases with distance from front to center by two to three times, but then almost in the entire sphere remains constant. Temperature increases from front to center, at first less sharply, while pressure decreases, and then, in region of constant pressure, very rapidly. Temperature increase in center is connected with the fact that near the center there are particles which were heated by very strong shock wave and possess high entropy. During adiabatic expansion to identical pressure, temperature is higher, the higher the entropy of the particles, i.e., the nearer to the center they are. Sharp decrease of density during approach to center is connected with temperature increase (pressure is constant).

Using condition of constancy of pressure over radius in region not too close to front, there can be found asymptotic distribution of gas-dynamic quantities as $r \to 0$. From equation of motion with $p(r) = \text{const}$, $\frac{\partial p}{\partial r} = 0$, it follows that $\frac{\partial u}{\partial t} + u\frac{\partial u}{\partial r} = 0$, i.e., $u = r/t$.

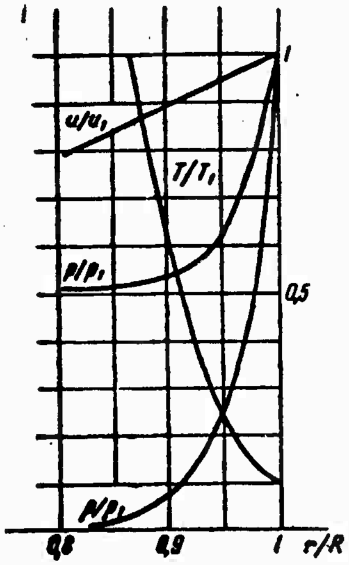

Fig. 1.50. Profiles of pressure, density, velocity, and temperature for strong point explosion in gas with $\gamma = 1.23$.

In order to find asymptotic law for density, let us turn to Legrange coordinate (see § 2). We will characterize given particle of gas by its initial radius r_0 (by "particle" we mean an elementary spherical shell with volume $4\pi r_0^2 dr_0$). At the moment of passage of the shock wave front, pressure in it is proportional to $p_1 \sim R^{-3} = r_0^{-3}$. Starting from this moment, particle r_0 is expanded adiabatically, so that at time t its density is equal to:

$$\rho(r_0 t) = \rho_1 \left[\frac{p(r_0 t)}{p_1(r_0)}\right]^{\frac{1}{\gamma}}.$$

But at given moment t, pressures in all particles located in "cavity" near the center are identical and are proportional to $p_c(t) \sim t^{-6/5}$. Therefore, asymptotic law for density in Lagrange coordinates is $\rho \sim r_0^3/\gamma t^{-6\gamma/5}$. Let us turn to Euler coordinate with help of definition (1.24): $\rho r^2 dr = \rho_0 r_0^2 dr_0$. Substituting here function for density and integrating, we will obtain dependence of Euler radius of given particle on time: $r \sim r_0^{(\gamma-1)/\gamma} t^{2/5\gamma}$. Eliminating from this expression r_0 with help of function $\rho(r_0 t)$, we will obtain the sought asymptotic law:

$$\rho \sim r^{\frac{3}{\gamma-1}} t^{-\frac{6}{5(\gamma-1)}} \text{ for } r \to 0.$$

Asymptotic law for temperature:

$$T \sim \frac{p_c}{\rho} \sim r^{-\frac{3}{\gamma-1}} t^{\frac{6}{5}\frac{(2-\gamma)}{(\gamma-1)}} \text{ for } r \to 0.$$

§ 26. Approximate Consideration of a Strong Explosion

Basic laws of process of strong explosion can be established with help of simple method of approximation proposed by G. G. Chernyy [7].

Let us assume that all of the mass of gas encompassed by blast wave is gathered in a thin layer at the surface of the front, density in which is constant and equal to density on front $\rho_1 = \frac{\gamma + 1}{\gamma - 1} \rho_0$. Thickness of layer Δr is determined from condition of conservation of mass:

$$4\pi R^2 \Delta r \rho_1 = \frac{4\pi R^3}{3} \rho_0; \quad \Delta r = \frac{R}{3} \frac{\rho_0}{\rho_1} = \frac{R}{3} \frac{\gamma - 1}{\gamma + 1}.$$

For instance, at $\gamma = 1.3$ $\Delta r/R = 0.0435$.

Inasmuch as the layer is very thin, velocity in it almost does not change and coincides with velocity of gas on the front u_1. Let us assume approximately that density in layer is infinitely great, and thickness accordingly is infinitesimal; mass is finite and is equal to mass M which was initially located in sphere of radius R: $M = \rho_0 4\pi R^3/3$. Let us designate pressure on inner side of layer by p_c. Let us assume that it composes fraction α of pressure on wave front $p_c = \alpha p_1$.

We will write second law of Newton for mass M:

$$\frac{d}{dt} M u_1 = 4\pi R^2 p_c = 4\pi R^2 \alpha p_1.$$

Mass $M = 4\pi R^3 \rho_0/3$ itself depends on time, so that with respect to time is differentiated not velocity, but momentum Mu_1. On the mass from within acts force $4\pi R^2 p_c$, since p_c is the force acting on 1 cm^2 of surface; force acting from without is equal to zero, since initial pressure of gas is disregarded. Expressing u_1 and p_1 in terms of velocity of front $D = dR/dt$ by the formulas (1.111), we will obtain

$$\frac{1}{3}\frac{d}{dt}R^3D = \alpha D^2R^2.$$

Noticing that

$$\frac{d}{dt} = \frac{d}{dR}\cdot\frac{dR}{dt} = D\frac{d}{dR}$$

and integrating the equation, we will find

$$D = aR^{-3(1-\alpha)},$$

where a is constant of integration. For determination of quantities a and α we use law of conservation of energy. Kinetic energy of gas is equal to $E_k = Mu_1^2/2$. Internal energy is concentrated in "cavity" bounded by our infinitely thin layer, pressure in which is equal to pressure p_c (actually this means that not strictly all of the mass is contained in the layer, but in the "cavity" there is also a small quantity of substance). Internal energy is equal to $E_T = \frac{1}{\gamma - 1}\frac{4\pi R^3}{3}p_c$. Thus,

$$E = \frac{1}{\gamma-1}\frac{4\pi R^3}{3}p_c + M\frac{u_1^2}{2}.$$

Again expressing $p_c = \alpha p_1$ and u_1 in terms of D and substituting D, we will obtain

$$E = \frac{4\pi}{3}\varrho_0 a^2\left[\frac{2\alpha}{\gamma^2-1} + \frac{2}{(\gamma+1)^2}\right]R^{3-6(1-\alpha)}.$$

Inasmuch as energy of explosion E is a constant, exponent of variable R should become zero. This gives $\alpha = 1/2$. The obtained equation determines constant a,

$$a = \left[\frac{3}{4\pi}\frac{(\gamma-1(\gamma+1)^2}{(3\gamma-1)}\right]^{\frac{1}{2}}\left(\frac{E}{\varrho_0}\right)^{\frac{1}{2}}.$$

From formula $D \sim R^{-3(1-\alpha)}$ with $\alpha = 1/2$ and formulas (1.111) there follow the laws already known to us:

$$D \sim R^{-\frac{3}{2}},\quad p_1 \sim R^{-3},\quad u_1 \sim R^{-\frac{3}{2}},\quad R \sim t^{\frac{2}{5}}.$$

With help of expression for a we will find proportionality factor in law $R \sim t^{2/5}$:

$$R=\left(\frac{5}{2}a\right)^{\frac{2}{5}}t^{\frac{2}{5}}=\left[\frac{75}{16\pi}\frac{(\gamma-1)(\gamma+1)^2}{(3\gamma-1)}\right]^{\frac{1}{5}}\left(\frac{E}{\varrho_0}\right)^{\frac{1}{5}}t^{\frac{2}{5}}=\xi_0\left(\frac{E}{\varrho_0}\right)^{\frac{1}{5}}t^{\frac{2}{5}}.$$

We will compare obtained approximate solution with exact solution. In approximate solution pressure in center is equal to half of pressure on front, independently of adiabatic index. In exact solution — $p_c = 0.35p_1$ for $\gamma = 1.4$; $p_c = 0.41p_1$ for $\gamma = 1.2$. Numerical coefficients ξ_0 in law of propagation of shock wave (1.108) in approximate solution are equal to: $\xi_0 = 1.014$ for $\gamma = 1.4$ and $\xi_0 = 0.89$ for $\gamma = 1.2$. In exact solution for the same values of γ, $\xi_0 = 1.033$ and 0.89 respectively.

As we see, approximate solution gives fairly good results.

§ 27. Remarks About Point Explosion, Taking into Account Counterpressure

In the later stage of propagation of a blast wave, when pressure in shock wave front becomes comparable with initial pressure of gas (more exactly, when p_1 becomes on the order of $[(\gamma + 1)/(\gamma - 1)]\, p_0$; see footnote on page 126), self-similar solution of problem about strong explosion loses validity.

Process in this stage no longer is self-similar, since in the problem there are characteristic scales of length and time, which it is possible to compose from quantity of total energy of explosion E and initial parameters of gas. As scale of length serves radius of sphere whose initial energy is comparable with energy of explosion $r_0 = (E/p_0)^{1/3}$. As scale of time serves time in which sound passes over this distance $t_0 = r_0/c_0$, where $c_0 = (\gamma p_0/\rho_0)^{1/2}$. Thus, for instance, during explosion in air of normal density ($\rho_0 = 1.25 \cdot 10^{-3}$ g/cm^3, $p_0 = 1$ atm, $c_0 = 330$ m/sec) for energy $E = 10^{21}$ erg, corresponding approximately to energy released during explosion of 20,000 tons of trotyl, scales are equal to $r_0 = 1$ km, $t_0 = 3$ sec.

Solution of problem about propagation of shock wave of point explosion, taking into account counterpressure, was obtained in a number of works [8-10] by means of numerical integration of partial differential equations of gas dynamics. All results of calculations, detailed tables, and graphs of distributions of gas-dynamic quantities at various moments of time can be found in these works, and also in fourth edition of book of L. I. Sedov [5].

We will be limited here only to certain remarks concerning qualitative character of the process.

With flow of time, amplitude of shock wave becomes less and less; pressure on front asymptotically approaches initial pressure of gas — atmospheric. Accordingly there decrease compression of gas in wave front and speed of wave propagation, which asymptotically approaches speed of sound c_0. Law of propagation $R \sim t^{2/5}$ gradually becomes law $R = c_0t$. When pressure in central region of blast wave becomes close to atmospheric, expansion of gas in this region is ceased and gas stops. Region of motion of gas is carried forward, nearer to shock wave front, which gradually becomes spherical wave of the same type as acoustic wave. Behind region of compression in such a wave there follows region of rarefaction, after which air arrives at its final state. Final state of layers far from center, through which shock wave has passed, since it is weak, little differs from initial state. Distributions of pressure, speed and density over radius at some later moment t have form depicted in Fig. 1.51. If we follow the change of pressure in time at a definite distance from center of explosion, then there will be obtained the picture shown in Fig. 1.52.

At the time t_1, when to the given place approaches shock wave front, pressure increases by a jump, then decreases; it drops to a magnitude lower than atmospheric pressure (positive and negative phases of pressure), and then returns to its initial magnitude.

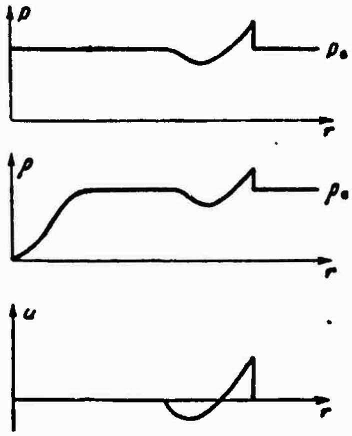

Fig. 1.51. Profiles of pressure, density and velocity at later stage of explosion, when shock wave becomes weak.

As was already said, final state of gas at large distances from center of explosion almost does not differ from initial state. At small distances, gas in final state turns out to be strongly rarefied and highly heated. This is connected with the fact that through particles located near the center, the shock wave has passed while very strong, and entropy of these particles is much higher than initial.

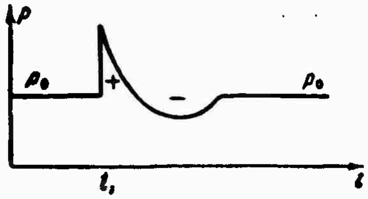

Fig. 1.52. Dependence of pressure on time at fixed point at large distance from center of explosion.

Asymptotic distributions of final density and temperature over radius near center can be found from condition of adiabatic expansion to atmospheric pressure of particles heated in strong shock wave front. Repeating calculations made at the end of § 25, but now without dependence of p_c on t, and considering $p_c = p_0 = \text{const}$, we will find the very same distributions over radius as $r \to 0$, as in the problem about a strong explosion $\rho \sim r^{3/(\gamma-1)}$, $T \sim r^{-3/(\gamma-1)}$.

Final distributions $\rho(r)$ and $T(r)$ are shown in Fig. 1.53. In heated region there is concentrated quite a considerable fraction of energy of explosion, on the order of several tens of percent (it depends on γ). This is the energy which went into irreversible heating of gas, which is connected with irreversibility of process of shock compression. Remaining energy passes forward together with shock wave and is dissipated in space. What happens to energy "sticking" in region of center will be discussed in Chapter IX (air in this region cools due to light emission).

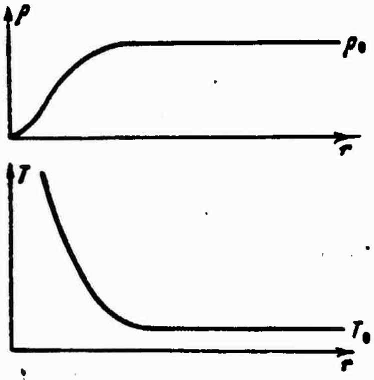

Fig. 1.53. Final distributions of density and temperature ($t \to \infty$) during strong explosion (under the assumption of adiabatic character of the process).

Later stage of propagation of blast wave has been studied theoretically and experimentally by many authors. Limiting laws of propagation of wave at large distances were found by L. D. Landau [11]. Empirical formula of M. A. Sadovskiy [12] for pressure on front in dependence on distance from center of explosion has great practical value. Let us note that law of similarity $p_1 = f\ (E^{1/3}/R)$ is valid also in later stage of propagation of shock wave, when $p_1 - p_0 \ll \rho_0$.

§ 28. Strong Explosion in Non-Homogeneous Atmosphere

Above there was considered problem about strong explosion in infinite homogeneous medium. As is known, atmosphere of Earth is not homogeneous; air density decreases with altitude, and, in a certain approximation, dependence of density ρ_0 on altitude h is described by barometric formula $\rho_0 = \rho_{00}e^{-h/\Delta}$, where ρ_{00} is density at sea level, and Δ is so-called altitude of standard atmosphere, which at the surface of Earth is equal approximately to 8.5 km.*

Let us see how shock wave of strong point explosion propagates in non-homogeneous atmosphere. We obviously will be interested in that stage in which wave has departed from point of explosion to distances comparable with scale of heterogeneity Δ; only then does there appear the influence of heterogeneity. Shock wave, as before, we assume to be strong (pressure behind front is much higher than pressure before the front).

Gas-dynamic process now no longer is self-similar (there is a scale of length Δ), and, moreover, motion is not one-dimensional, but two-dimensional. In cylindrical coordinates with vertical axis passed through point of explosion, motion depends on coordinate z and radius r. Complete solution of gas-dynamic problem can be found only by means of numerical integration of equations of gas dynamics. However, it is possible to obtain an idea of the character of propagation of shock wave and shape of its surface on the basis of simple considerations, which was done by A. C. Kompaneyets in work [13]**.

Let us assume that, as for an explosion in a homogeneous medium, pressure is equalized almost over the entire volume encompassed by the blast wave, and on the front is constant along surface of front and proportional to mean pressure, i.e., to the ratio of energy of explosion to the entire volume Ω:

$$p_1 = (\gamma - 1)\lambda \frac{E}{\Omega}. \qquad (1.114)$$

---

*In reality terrestrial atmosphere is not strictly exponential, since temperature of air changes with altitude. Scale Δ, which is determined as $\Delta = -(d \ln \rho/dh)^{-1}$, changes in interval from 6 to 15 km at altitudes below 150 km. Above 150 km, scale Δ becomes still larger.

**See also [14].

Here $\lambda(\gamma)$ is numerical coefficient, which for estimate can be taken, for instance, from solution of problem about explosion in a homogeneous medium. Let us assume that equation of surface of shock wave front in cylindrical coordinates is $f(z, r, t) = 0$. By differentiating this equation, we will obtain

$$\frac{\partial f}{\partial z}dz+\frac{\partial f}{\partial r}dr+\frac{\partial f}{\partial t}dt=0$$

or

$$\frac{\partial f}{\partial z}D_z+\frac{\partial f}{\partial r}D_r=D\nabla f=-\frac{\partial f}{\partial t},$$

where D_z and D_r are vector components of velocity of front D. Normal component of velocity of front is expressed by known formula

$$D_n=-\frac{\partial f}{\partial t}\Big/|\nabla f|.$$

But, according to condition on front of strong shock wave,

$$D_n=\left(\frac{p_1}{\rho_0}\frac{\gamma+1}{2}\right)^{\frac{1}{2}},$$

where ρ_0 is density before front at given point of surface.

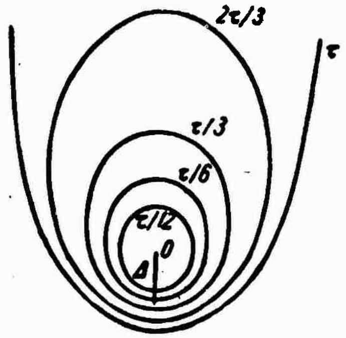

Fig. 1.54. Cross section of surfaces of shock wave front for strong explosion at a great altitude along the vertical plane passing through point of explosion. There are shown consecutive moments of time. On segment Δ, density of atmosphere changes by e times.

From the last two expressions we have:

$$\left(\frac{p_1}{\rho_0}\frac{\gamma+1}{2}\right)^{\frac{1}{2}}=-\frac{\partial f}{\partial t}\Big/|\nabla f|. \qquad (1.115)$$

We substitute here pressure p_1 by formula (1.114) and express volume Ω in the form of integral $\Omega = \int d\Omega$ with help of equation of surface of front bounding volume Ω.

Thus equation $f(z, r, t)$ will be considered to be solved for radius $r = r(z, t)$. Atmosphere will be considered strictly exponential. Such an operation leads to partial differential equation for the sought function $r = r(z, t)$. which is solved in work [13].

Evolution of surface of shock wave front is seen from Fig. 1.54, borrowed from work [13], on which there are depicted cross sections of wave along vertical plane passing through point of explosion (through axis z). In Fig. 1.54 there are shown sections in consecutive moments of time. Wave which in the beginning is spherical gradually takes egg-shaped form, and then, after a finite time τ, goes upwards to infinity, as if "breaking through" the atmosphere. This characteristic time τ is equal to

$$\tau=\beta\sqrt{\frac{32\pi\Delta^5\rho^*}{\lambda E(\gamma^2-1)}},$$

where β is numerical constant equal approximately to $\beta \approx 1.4$, and ρ^* is density of atmospheric air at altitude of explosion. By moment $t = \tau$ the wave goes downwards to a distance of $1.38\ \Delta$, and along horizontal to a distance of $2.04\ \Delta$. Wave goes upwards to an infinite distance in a finite time, since during upward motion through more and more rarefied air, shock wave is accelerated to infinite velocity.

During motion downwards, in the direction of dense air, wave is decelerated the fastest of all. At the time $t = \tau$, the volume of air enveloped by the shock wave becomes infinite; pressure by formula (1.114) becomes zero, and solution loses validity. Obtained solution is applicable only under the condition that shock wave is strong, when

$$\frac{p_1}{p_0}\sim\frac{E}{p_0\Omega}\sim\frac{E}{p_0R^3}\gg 1,$$

where R is characteristic dimension of region enveloped by shock wave, and p_0 is atmospheric pressure.

Heterogeneity of atmosphere has an effect only when wave goes to distances comparable with scale Δ, i.e., to distances on the order of 10 km. Thus the above described evolution of surface of front will occur only during explosions of great power at a great altitude, where density and pressure are low.

For instance, at altitude h = 100 km, p_0 is on the order of 10^{-6} atm = 1 bar, and $p_1/p_0 > 100$ at distance of $R \approx 10$ km only for explosions with energy $E > 10^{20}$ erg.

For explosion with not excessively great power at low altitude, shock wave attenuates at distances much less than Δ, and process of strong explosion proceeds practically in a homogeneous atmosphere.

§ 29. Adiabatic Dispersion of a Gas Sphere into a Vacuum

Let us become acquainted with another gas-dynamic problem with which it will be necessary for us to deal in the future (in Chapter VIII): the problem about dispersion of gas into a vacuum.

Let us imagine a gas sphere occupying at the initial moment a spherical volume of radius R_0. Let us assume that, for definiteness, at initial moment gas is at rest and fills volume uniformly with density ρ_0 (total mass of gas is $M = \rho_0 4\pi R_0^3/3$). Initial pressure of gas also is considered to be constant and equal to p_0, so that total energy of gas is $E = \frac{1}{\gamma - 1} p_0 \frac{4\pi R_0^3}{3}$ (gas is assumed to be ideal with constant heat capacity). At time t = 0 there is removed the partition restraining the gas, and the latter starts to be expanded into the vacuum without restraint.

After removal of partition there occurs disintegration of shock and through gas to center there propagates a rarefaction wave. Front layers of gas are expanded into vacuum with maximum velocity of outflow $u_{max} = \frac{2}{\gamma - 1} c_0$. When rarefaction wave reaches center, the motion - dispersion — involves all of the substance. In process of adiabatic dispersion, due to work of expansion accomplished by gas, substance accelerates, and its initial internal energy E gradually becomes kinetic energy of radial motion. It is possible to show (see [15]) that during isentropic dispersion (and our problem is isentropic, since at the initial moment, in virtue of constancy of pressure and density over radius, entropies of all particles are identical, perturbations from internal regions of sphere do not reach the front boundary, so that it moves with constant speed $u_{max} = \frac{2}{\gamma - 1} c_0$. Law of motion of boundary of gas sphere is $R = \frac{2}{\gamma - 1} c_0 t + R_0$. It is not possible to find exact analytic solution of problem at hand, since problem is not self-similar, and it is necessary to solve system of partial differential equations, which it is possible to do analytically only in very rare cases. The fact that problem is not self-similar is easy to verify by noticing that there is a characteristic scale of length — initial radius of sphere R_0.

However, this problem possesses the property that with flow of time, motion asymptotically becomes self-similar. Really, in the stage of large expansion at $R \gg R_0$, role of initial parameter of length becomes less and less important, since scale of length R_0 becomes very small as compared to characteristic scale of flow — the actual radius of the sphere R. Motion of gas with flow of time as it were "forgets" about initial radius R_0. Nevertheless, motion does not completely "forget" about initial conditions, and in this there appears essential non-self-similarity established in the considered process.

Let us consider asymptotic behavior of solution as $t \to \infty$.

Force acting per unit of mass of gas thus tends to zero. Indeed, this force $-\frac{1}{\rho}\frac{\partial p}{\partial r}$ in order of magnitude is equal to $-p/\rho R$, where p and ρ are certain average pressure and density over mass at time t. But average pressure p proportionally to ratio of thermal energy of all of the gas to its volume $p \sim E_{therm}/R^3$ and in any case is less than E/R^3. Average density $\rho \sim 1/R^3$; therefore force tends to zero in any case not slower than $1/R$. In fact, force decreases as $R \to \infty$ faster than $1/R$, since thermal part of energy decreases during adiabatic expansion: $E_{therm} \sim M\varepsilon \sim M\frac{p}{\rho} \sim \rho^{\gamma-1} \sim R^{-3(\gamma-1)}$. Hence $p \sim \sim E_{therm}/R^3 \sim R^{-3\gamma}$, decreases as $R^{-3\gamma+2} = R^{-1-3(\gamma-1)}$. Equation of motion in the limit as $t \to \infty$, $R \to \infty$ acquires asymptotic form:

$$\frac{du}{dt} = \frac{\partial u}{\partial t} + u\frac{\partial u}{\partial r} = -\frac{1}{\rho}\frac{\partial p}{\partial r} \sim \frac{1}{R^{1+3(\gamma-1)}} \to 0,$$

i.e., speeds of all particles tend to constant values, where $u = r/t$.

As $t \to \infty$ dispersion acquires inertial character.

This follows directly from condition of conservation of total energy of gas E. Total energy is composed of thermal and kinetic energies, but thermal part of energy during expansion asymptotically tends to zero; consequently, kinetic energy tends to E, and average speed of gas mass asymptotically tends to constant limiting value $u_\infty = \sqrt{2E/M}$, which is in a definite numerical ratio with speed of boundary:

$$u_{max} = \frac{2}{\gamma-1}c_0 = \frac{2}{\gamma-1}\sqrt{\gamma\frac{p_0}{\rho_0}} = \frac{2}{\gamma-1}\sqrt{\gamma(\gamma-1)\varepsilon_0} = \sqrt{\frac{4\gamma}{\gamma-1}\frac{E}{M}} = \sqrt{\frac{2\gamma}{\gamma-1}}u_\infty$$

(for instance, in monatomic gas $\gamma = 5/3$ and $u_{max} = 2.9u_\infty$). By substituting asymptotic solution for velocity $u = r/t$ in continuity equation, we are convinced that it is satisfied by the following density function:

$$\rho = \frac{f\left(\frac{r}{t}\right)}{t^3},$$

where f is an absolutely arbitrary function of r/t. Inasmuch as radius of boundary of sphere is equal to $R = u_{max}t$, this formula can be rewritten in the form

$$\rho = \frac{\varphi(r/R)}{R^3}.$$

Asymptotic distribution of density over radius does not change with flow of time; it only is stretched in conformity with increase of R, while remaining similar to itself, self-similar. Actually, if in the gas there do not act any forces, and every particle flies with constant speed by inertia, then no redistribution of mass occurs, and profile of density remains constant.

However, internal non-self-similarity of problem is evident in the fact that this asymptotic distribution of density cannot be found from equations of asymptotic motion, which permit any distribution.

Distribution of density is formed in the early stage, when in the gas there act forces of pressure. By the time when gas is strongly expanded, it is, as it were, "frozen." Distribution of density depends on initial conditions and can be found only on the basis of complete solution of the problem.

As already has been noted, exact solution of problem with initial conditions $\rho_0(r)$ = const, $p_0(r)$ = const, $u = 0$ is impossible to find in analytic form. Approximate solution is possible to construct, if we proceed from consideration of the analogous two-dimensional problem about dispersion into vacuum of a gas layer of finite mass with constant initial distributions, which can be solved. This approximate solution is given in book of K. P. Stanyukovich [15]; it has the form:

$$\rho = \frac{A}{R^3}\left(1 - \frac{r^2}{R^2}\right)^{\alpha}, \quad \alpha = \frac{3-\gamma}{2(\gamma-1)}, \quad R = u_{\max}t,$$

where solution is valid only for integral values $\alpha = 0, 1, 2, 3, \ldots$, which correspond to following series of values of adiabatic index: $\gamma = 3, 5/3, 7/5, 9/7 \ldots$.

Constant A can be determined from condition of conservation of mass if we integrate density function over entire volume of sphere. Corresponding formula is given in [15].

§ 30. Self-Similar Regimes of Dispersion of Sphere into a Vacuum

There exists a class of solutions of problem about dispersion of gas sphere into a vacuum in which distribution of all gas-dynamic quantities are strictly self-similar, i.e., from the very beginning depend on radius r in the form of ratio of r to radius of boundary of sphere R and do not contain any other dependence on r. To these solutions lead not any initial distributions of quantities over radius, but only those which satisfy a definite relationship.

This class of solutions is characterized by linear distribution of velocity over radius (such solutions were investigated by L. I. Sedov [5]):

$$u = rF(t) = \dot{R}\frac{r}{R}, \tag{1.116}$$

where function of time F(t) is expressed in terms of speed of boundary of sphere $\dot{R} = dR/dt$. By substituting this formula in equation of motion, we will obtain relationship

$$\frac{\partial p}{\partial r} = -\rho r(\dot{F} + F^2), \tag{1.117}$$

which must be satisfied by distributions of p and ρ over radius during the entire process, including at the initial moment of time. Only under this condition will the solution belong to the considered class.

Let us consider two concrete examples of such solutions.

1. Let density ρ be constant over all of volume and not depend on radius

$$\rho = f(t) = \frac{M}{4\pi R^3/3}. \tag{1.118}$$

It is easy to verify that assignment of functions of density and speed in form (1.118), (1.116) automatically satisfies continuity equation for arbitrary dependence R(t). Substituting (1.118) in

(1.117) and integrating, we will obtain parabolic distribution of pressure over radius

$$p = p_0(t)\left(1 - \frac{r^2}{R^2}\right), \qquad (1.119)$$

which should be assigned from the very beginning so that condition (1.117) is satisfied. As we see, the problem is not isentropic, since densities for all particles are identical, and pressures are different. Substitution of p and ρ into entropy equation gives relation between unknown functions: pressure in center $p_0(t)$ and radius of sphere R(t):

$$p_0(t) = A\rho^{\gamma} = A\left(\frac{3M}{4\pi}\right)^{\gamma}\frac{1}{R^{3\gamma}}, \qquad (1.120)$$

where A is a constant depending on initial entropy in center of sphere. Substituting, finally, (1.118), (1.119), (1.120) into equation of motion (1.117), we will obtain second order differential equation for law of motion of boundary of sphere R(t). Solving it with initial condition $t = 0$, $R = R_0$, $\dot{R} = \dot{R}_0$, we will find complete solution of the problem. In particular, we may assume that at initial moment the gas is at rest: $\dot{R}_0 = 0$.

If we are interested in asymptotic behavior as $t \to \infty$, it is immediately possible to set $R = \text{const} = u_1$, where u_1 is limiting velocity of boundary of sphere (solution of differential equation, naturally, gives $R \to \text{const}$ as $t \to \infty$). Quantity u_1 can with the help of radial distributions of ρ and u be calculated from condition of conservation of energy, considering that as $t \to \infty$ all energy becomes kinetic. We obtain thus:

$$u_1 = \sqrt{\frac{5}{3}}\sqrt{\frac{2E}{M}} = \sqrt{\frac{5}{3}}\,u_{\infty}, \qquad (1.121)$$

where u_{∞} as before is defined as square root of average of square of velocity over mass $u_{\infty} = \sqrt{\overline{u^2}} = \sqrt{2E/M}$.

2. Let us assume that entropies of all particles are identical (isentropic motion), i.e., $S(r, t) = \text{const}$, $p/\rho^{\gamma} = A = \text{const}$ (A is entropy constant). Substitution of $p = A\rho^{\gamma}$ in relationship (1.117) leads to following profiles of pressure and density:

$$\rho = \rho_c \left(1 - \frac{r^2}{R^2}\right)^{\frac{1}{\gamma - 1}}, \tag{1.122}$$

$$p = A\rho_c^{\gamma} \left(1 - \frac{r^2}{R^2}\right)^{\frac{\gamma}{\gamma - 1}}, \tag{1.123}$$

which naturally have to be assigned from the very beginning.

Density in center ρ_c can be determined by integrating density over volume and equating integral to mass: this gives, as usual, $B \sim M/R^3$, with numerical proportionality factor depending on γ. Relation (1.117) leads after substitution of (1.122), (1.123) to second order equation for $R(t)$. Limiting value of speed of boundary u_1 can be obtained from condition of conservation of energy:

$$E = \int_0^R \frac{\rho u^2}{2} 4\pi r^2 dr,$$

if we substitute in integral ρ by formula (1.122) and $u = u_1 r/R$.

This gives relation between u_1 and $u_\infty = \sqrt{2E/M}$, where proportionality factor also depends on γ. Both coefficients are expressed by definite integrals, which are calculated with the help of gamma-functions.

Let us give numerical results. For $\gamma = 5/3$ $\rho_c = 3.4\bar{\rho}$, $u_1 = 1.64\, u_\infty$; for $\gamma = 4/3$ $\rho_c = 6.6\bar{\rho}$, $u_1 = 1.92\, u_\infty$, where $\bar{\rho} = M/(4\pi R^3/3)$ is average density over volume. In the limit as $t \to \infty$ $R \approx u_1 t$.*

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*In work [17] there are reported certain results of numerical solution of equations of gas dynamics for problem about isentropic dispersion of sphere into vacuum under uniform initial conditions (at $t = 0$ gas in sphere is at rest, its density and pressure are constant over radius). Unfortunately, in the work there is not given asymptotic profile of density, but there is given graph of $\rho_c(t)$. It is clear that with passage of time the dependence tends to $\rho_c \sim 1/t^3$, where coefficient in this limiting law turns out to be altogether 1.22 times as great as in the self-similar solution described here.

Let us note work of V. S. Imshennik [16], in which there is considered problem about isothermal dispersion of gas into a vacuum.

Literature

1. L. D. Landau and Ye. M. Lifshits. Mechanics of solid matter. State Technical Press, 1954.

2. Ya. B. Zel'dovich. Theory of shock waves and an introduction to gas dynamics. Publishing House of Academy of Sciences of USSR, 1946.

3. N. Kotchine, Rendiconti del Circolo Mat. de Palermo 50, 1926. A. V. Rossi, N. A. Kibel, N. Y . Kochine. Theoretical hydromechanics. Part II, ONTI, 1937.

4. L. I. Sedov. DAN SSSR 42, No. 1 (1946); Applied mathematics and mechanics. 10, No. 2 (1946).

5. L. I. Sedov. Methods of similarity and dimension in mechanics. 4th edition, State Technical Press, 1957.

6. G. Taylor. Proc. Roy. Soc., 201, 175 (1950).

7. G. G. Chernyy. DAN SSSR, 112, 213 (1957).

8. J. Neumann, and H. Coldstine. Comm. Pure and Appl. Math., 8, N 2, 327 (1955).

9. H. J. Brode. J. Appl. Physics 26, N 6, 766 (1955).

10. D. Ye. Okhotsimskiy, I. L. Kondrasheva, Z. P. Vlasova, and R. K. Kazakova. Proceedings of the Mathematical Institute of the Academy of Sciences of USSR, 50, 1957.

11. L. D. Landau. Applied mathematics and mechanics, 9, No. 4, 286 (1945).

12. M. A. Sadovskiy. Collection, Physics of explosion. Publishing House of Academy of Sciences of USSR, No. 1, 1952.

13. A. S. Kompaneyets. DAN, 130, 1001 (1960).

14. E. I. Andriankin, A. M. Kogan, A. S. Kompaneyets, and V. P. Kraynov. PMTF, No. 6 (1962).

15. K. P. Stanyukovich. Transient motions of a solid medium. State Technical Press, 1955.

16. V. S. Imshennik. DAN 131, 1287 (1960).

17. P. Molmud. Phys. Fluids 3, 362 (1960).

18. G. Kurant and K. Friedrichs. Supersonic flow and shock waves, IL, 1950.

CHAPTER II

THERMAL RADIATION AND RADIANT HEAT EXCHANGE IN A MEDIUM

§ 1. Introduction and Basic Ideas

Up to recent times high temperatures of the order of tens and hundreds of thousands or millions of degrees interested mainly astrophysicists. Theory of radiation transfer and radiant heat exchange was created and developed as a necessary element for understanding of processes occurring in stars, and explanation of observed luminosity of stars. To a considerable degree this theory is also transferrable to other high-temperature objects, with which physics and technology of today must deal. In this chapter we will become acquainted with fundamentals of theories of thermal radiation, radiant transfer of energy, theory of luminosity of heated bodies, and will formulate equations describing hydrodynamic motion of substance under conditions of intense radiation. In the account of these topics we will be oriented toward "terrestrial" applications, while dwelling on certain aspects which are not so important for astrophysics, or which do not even appear in this area.*

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*It is possible to become acquainted in more detail with problems of theory of radiation transfer and its applications to astrophysics in books of V. A. Ambartsumyan and others [1], Unsöld [2], E. R. Mustel' [3].

We will recall basic concepts and definitions of the theory of thermal radiation. Radiation is characterized by frequency of oscillations of electromagnetic field ν or wave length λ related with frequency through velocity of light $\lambda = c/\nu$. Subsequently, we will always deal with media in which index of refraction is very close to unity, so that by c we will mean velocity of light in a vacuum, equal to $c = 3 \cdot 10^{10}$ cm/sec. From quantum point of view, radiation is considered as a collection of particles, photons or light quanta, whose energy is connected with frequency of equivalent field by means of Planck's constant $h = 6.62 \cdot 10^{-27}$ erg·sec. Usually energy of a quantum $h\nu$* is measured in electron volts. One electron volt is the energy which is acquired by an electron during passage through a potential difference of 1 volt; 1 electron volt (1 ev) is equal to $1.6 \cdot 10^{-12}$ erg. Frequently in electron volts is measured temperature. Temperature T of 1 electron volt corresponds to energy of $kT = 1.6 \cdot 10^{-12}$ erg, where $k = 1.38 \cdot 10^{-16}$ erg/degree — the Boltzmann constant:

$$T_{\text{эв}} = \frac{kT^\circ}{1{,}6 \cdot 10^{-12}} = \frac{T^\circ}{11600},$$

i.e., temperature of 1 ev is equal to 11 600° K.

In electromagnetic scale of frequencies (wave lengths) or, so to speak, in spectrum of radiation, usually there are distinguished several very unclearly defined ranges, which have definite names: radio wave, infrared, visible, ultraviolet, x-radiation, γ-quanta. This division was made historically and does not have any strict physical foundation. Certain frequencies intermediate between intervals are even difficult to refer to one or the other heading. An exception

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*In Quantum theory it is accepted to use instead of frequency ν "circular" frequency $\omega = 2\pi\nu$ and, accordingly, Planck's constant $h = h/2\pi$. In this book we will use quantities ν and h, as this is accepted in theory of radiation transfer and astrophysics.

is only the more or less definite, visible part of the spectrum: $\lambda \sim 7500\text{-}4000\text{Å}$, $h\nu \sim 1.7\text{-}3.13$ ev. In theory of thermal radiation it is proven that in state of thermodynamic equilibrium of radiation with substance, maximum of energy of spectrum with respect to frequency belongs to frequency ν, which is related with temperature by the formula $h\nu = 2.82\ kT$. It is possible to say that frequency ν is most characteristic for a body with temperature $T = h\nu/2.82\ k$; therefore, comparison of frequency and temperature ranges immediately gives an idea of to what temperatures a given region of the spectrum correspons. Visible radiation is characteristic for bodies with temperatures of the order of $7000^\circ\text{-}13000^\circ$ K.

Electromagnetic field or light quanta possess not only energy, but also momentum. Momentum of quantum $h\nu$ in absolute value is equal to $h\nu/c$. Direction of motion of quantum coincides with vector of energy flow of field — Poynting vector.

Field of radiation filling space is described by distribution of intensity of radiation over frequencies in space and along directions of transfer of radiant energy. If we speak about radiation as a collection of particles — light quanta — then field can be characterized by distribution function of quanta, which is fully analogous to distribution function of any other particles. Let us assume that $f(\nu, \mathbf{r}, \mathbf{\Omega}, t)\, d\nu\, d\mathbf{r}\, d\mathbf{\Omega}$ is number of light quanta in spectral range from ν to $\nu + d\nu$, which are located at time t in element of volume $d\mathbf{r}$* near point $\mathbf{r}$ and have direction of motion in elementary solid angle $d\mathbf{\Omega}$ near unit vector $\mathbf{\Omega}$. Function f is called distribution function.

Every quantum possesses energy $h\nu$ and moves with velocity c; therefore, the quantity

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*Linear dimensions of elementary volume $d\mathbf{r}$ are assumed to be much larger than wave length λ.

$$I_\nu(r, \Omega, t)\, d\nu\, d\Omega = h\nu c f(\nu, r, \Omega, t)\, d\nu\, d\Omega]$$

is quantity of radiant energy in spectral range $d\nu$ flowing in 1 sec through an element of 1 cm^2, which is placed at point **r** perpendicular to directions of propagation of energy, which lie in elementary solid angle $d\Omega$ near vector Ω. I_ν is called spectral intensity of radiation. Assigning functions I_ν or f completely determines field of radiation. Quantity of radiant energy contained in spectral interval $d\nu$ and located in 1 cm^3 of space at point **r** at time t, or spectral density of radiation, is equal to

$$U_\nu(r, t) = h\nu \int_{(4\pi)} f\, d\Omega = \frac{1}{c} \int_{(4\pi)} I_\nu\, d\Omega. \tag{2.1}$$

Let us imagine a unit element with direction of normal **n**. Quanta intersect it from the left to the right and from the right to the left. Quantity of radiant energy in interval $d\nu$ flowing in 1 sec through the element from the left to the right is equal to $h\nu c \int_{2\pi} f \cos\vartheta\, d\Omega$, where ϑ is angle between direction of motion of quanta Ω and normal **n**; integral is taken over right hemisphere, as the base of which serves the element of area (Fig. 2.1). Integral over left hemisphere is equal to quantity of energy flowing from the right to the left. Difference between unidirectional fluxes from the left to the right and from the right to the left gives total spectral energy flow through this element of area. Inasmuch as $\cos\vartheta$ has different signs in right and left hemispheres, spectral energy flow through element with normal **n** is equal to

$$S_\nu(r, t, n) = h\nu c \int_{(4\pi)} f \cos\vartheta\, d\Omega = \int_{(4\pi)} I_\nu \cos\vartheta\, d\Omega, \tag{2.2}$$

where integral is taken over entire solid angle.

Flux is a vector quantity. The written expression (2.2) is a projection of flux vector onto direction **n**. The vector of spectral flux itself is equal to

$$S_\nu = \int I_\nu \mathbf{\Omega}\, d\Omega, \tag{2.3}$$

where $\mathbf{\Omega}$ is unit vector of direction of motion of quanta.

With isotropic distribution of radiation, when distribution function f and intensity I_ν do not depend on direction $\mathbf{\Omega}$, density of radiation is equal to

$$U_\nu = 4\pi h\nu f = \frac{4\pi}{c} I_\nu, \tag{2.4}$$

and there is no flux: $S_\nu = 0$ and projections onto all directions are also equal to zero (since in every direction there is transfered exactly as much energy as in the opposite direction).

Total intensity, density, and flux of radiation are obtained from their spectral counterparts by integration of them over the entire spectrum of frequencies:

$$I = \int_0^\infty I_\nu d\nu, \quad U = \int_0^\infty U_\nu d\nu, \quad S = \int_0^\infty S_\nu d\nu. \tag{2.5}$$

Let us introduce now the idea of optical characteristics of a substance.*

Amount of energy spontaneously radiated in 1 cm^3 of substance in 1 sec in the spectral interval $d\nu$ is called spectral emittance or radiation factor J_ν. Usually gases radiate light in all directions equally, isotropically, since atoms, molecules, ets., are oriented and move in space in a random manner. Therefore amount of energy radiated in solid angle $d\Omega$ in some direction is equal simply to $j_\nu\, d\Omega = J_\nu\, d\Omega/4\pi$ (j_ν is calculated per unit solid angle).

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*Here and subsequently, when using terms "light," "light quanta," "optical" properties, we will not be limited, as is accepted in everyday useage, only to visible part of spectrum, but will carry these terms to any frequencies.

Sometimes emittance is referred not to unit of volume, but to a unit of mass. In order to obtain corresponding magnitudes, it is obviously necessary to divide J_ν or j_ν by density of substance ρ.

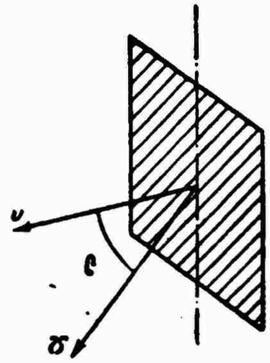

Fig. 2.1. Concerning the derivation of the formula for flux of radiant energy.

If through substance there passes a beam of light, it is attenuated along its path. Attenuation occurs due to absorption of quanta, as well as due to their scattering, i.e., deflection from initial direction. Relative attenuation of parallel beam on element of path dx is proportional to this element, i.e.,

$$dI_\nu = -\mu_\nu I_\nu dx. \tag{2.6}$$

Intensity of beam decreases after passage over distance x from point x = 0 to point x by exponential law

$$I_\nu = I_{\nu 0} \exp\left[-\int_0^x \mu_\nu dx\right]. \tag{2.7}$$

Attenuation factor μ_ν is composed of coefficient of absorption $\varkappa_{\nu a}$* and scattering coefficient $\varkappa_{\nu s}$. Reciprocals are mean free paths of light: total $l_\nu = 1/\mu_\nu$, with respect to absorption $l_{\nu a} = 1/\varkappa_{\nu a}$ and with respect to scattering $l_{\nu s} = 1/\varkappa_{\nu s} (l = (l_{\nu a}^{-1} + l_{\nu s}^{-1})^{-1})$. Mean free paths characterize attenuation of beam of light with respect to the corresponding process per unit of path. Coefficients which are referred not to unit of path, but to unit of mass are spoken of as mass coefficients. Mass coefficients are equal respectively to μ_ν/ρ, $\varkappa_{\nu a}/\rho$, $\varkappa_{\nu s}/\rho$.

Mean free path is the average distance which a quantum passes over before it is absorbed, scattered, etc. But quantum travels with

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*We now digress from processes of stimulated emission, about which we will be concerned below, and imply by $\varkappa_{\nu a}$ the coefficient of true absorption.

speed c, and therefore average time of "life" of quantum with respect to a given event is equal to mean free path divided by velocity of light l/c. For instance, if on element of path, dx there is absorbed fraction $dx/l_{\nu a}$ of quanta, then during the time dt there is absorbed fraction $c\,dt/l_{\nu a}$.

Attenuation of beam of light is characterized by product of attenuation factor and mean free path. Dimensionless quantity

$$\tau_\nu = \int_0^x \mu_\nu\,dx, \quad d\tau_\nu = \mu_\nu\,dx \tag{2.8}$$

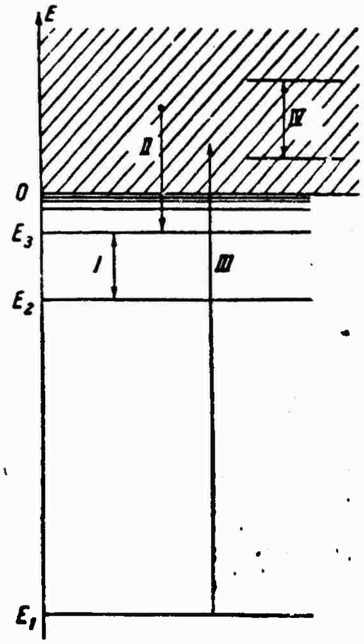
is called optical thickness of layer x with respect to light of frequency ν. Beam of light is attenuated by e times on an optical thickness equal to unity. In the case when scattering can be disregarded, optical thickness is

$$\tau_\nu = \int_0^x \varkappa_{\nu a}\,dx, \quad d\tau_\nu = \varkappa_{\nu a}\,dx. \tag{2.9}$$

§ 2. Mechanisms of Emission, Absorption and Scattering of Light in Gases

Light quanta are radiated and absorbed during transitions of electrons in atomic systems: atoms, molecules, ions, electron-ion plasma, from one energy state to another. During absorption of a quantum there occurs excitation of the atom, molecule, etc. So that emission of quantum occurs, it is necessary preliminarily to excite atom; atom loses excitation energy, transmitting it to the emitted quantum. Emittance is higher, the larger the number of excited atoms, i.e., the higher the temperature.

In Fig. 2.2 there is depicted energy level diagram of simplest atomic system, consisting of proton and electron, which in bound state form an atom of hydrogen. As zero energy is taken, as usual, the boundary between free and bound state of electron, so that in bound state energy is negative. In bound state electron can be only at definite, discrete energy levels. Ground state of proton — electron system has energy $E_1 = -13.5$ ev, which is in absolute value to ionization potential of atom of hydrogen. In free state with positive energy (ionized atom of hydrogen) electron can possess any energy, so that energy spectrum is continuous.



.Fig. 2.2. Energy level diagram of proton-electron system. $E_1 = -13.5$ ev is ground state of atom of hydrogen, E_2, E_3 are levels with principal quantum numbers n = 2.3. E = 0 corresponds to boundary between line and continuous spectra. Arrows show possible types of transitions: I) bound-bound; II) capture of electron by proton; III) ionization of atom; IV) free-free.

In qualitative sense, energy spectrum of complicated atomic systems does not differ from spectrum of the simplest system.

All electron transitions can be, as this is accepted in astrophysics, subdivided into three groups according to the criterion of continuity or discreteness of energy spectrum of initial and final states of the atomic system: into bound-bound, bound-free, and free-free (all allowed transitions are shown in Fig. 2.2 by arrows).

Bound-bound transitions include transitions of electrons within atoms, molecules and ions from one discrete level to another. In virtue of discreteness of energy levels of bound state of electrons, during such transitions there are emitted and absorbed line spectra. In molecules, when simultaneously with electron transition there occurs change of state of vibrational and rotational motions, there are obtained band spectra.*

During bound-free transitions, electron as a result of absorption of quantum obtains energy exceeding binding energy of it in the atom, molecule, or ion and becomes free — there occurs photo-ionization. Excess of quantum energy over binding energy is turned into kinetic energy of free electron. Reverse transitions — capture of free electrons by ions in ionized gas (photo-recombination) — lead to emission of quanta. Inasmuch as free electron can possess arbitrary (positive) energy, bound-free transitions given continuous absorption and radiation spectra.

It is necessary to note that not any quantum may cause a photoeffect in an atom which is in a definite state. Energy of quantum should exceed binding energy of electron in this state. However, any, even the smallest quantum, can pull an electron from a sufficiently strongly excited atom, since with increase of excitation the electron becomes more and more weakly bound.

In an ionized gas (plasma), a free electron traveling in electrical field of ion can emit a quantum without losing besides all of its kinetic energy and remain free, or absorb a quantum and obtain additional kinetic energy. These free-free transitions are frequently called "braking"** transitions, since during emission the electron is decelerated in field of ion, losing part of its own energy in radiation. These processes also give a continuous spectrum of radiation

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*In molecules sometimes there occur transitions accompanied by change of only vibrational and rotational states without change of electronic state. Then there are emitted or absorbed quanta of very low energy, which lie in infrared region of spectrum. At temperatures of the order of several thousand degrees and above, they play an insignificant role.

**Trans. Ed. quotes.

and absorption.

These processes can occur also during flight of an electron in field of a neutral atom. In distinction from field of ion, field of neutral atom very rapidly decreases with distance; therefore for process of emission or absorption of light, there is necessary close approach of electron to atom. Probability of "braking" process with participation of neutral atom is much less than with participation of ion.

Coefficients of bound-bound and bound-free absorption are proportional to number of absorbing atoms located in 1 cm^3 of gas N. Magnitude of coefficient referred to one absorbing atom depends only on properties of atom, degree of its excitation, frequency of quantum, i.e., is a characteristic of the actual atom. This quantity $\varkappa_{\nu a}/N = \sigma_\nu$ has dimension of cm^2 (dimension of $\varkappa_{\nu a}$ is 1/cm, dimension of N is $1/cm^3$) and has the name of effective absorption cross section. Its physical meaning is easy to understand by means of the following reasoning. Let us assume that parallel beam of light of frequency ν with cross section of 1 cm^2 passes through absorbing gas. Absorption can be imagined thus as if every atom is replaced by some little opaque disk perpendicular to direction of beam; on hitting this "disk" the quantum sticks (is absorbed).

If area of every disk is equal to σ_ν, and number of disks (atoms) per cm^3 is N, then total area of all disks, located in layer of gas with area of 1 cm^2 and thickness dx, is equal to 1 cm^2 $N\sigma_\nu$ dx. Let us select dx so small that disks located in layer do not overlap. Then, obviously, during passage of light through such a layer there will "stick" a fraction of the quanta which is equal to ratio of opaque area $N\sigma_\nu$ dx cm^2 to total area 1 cm^2; i.e., $dI_\nu = -I_\nu N\sigma_\nu \, dx$. Remembering definition of coefficient of absorption (see formula (2.6)), we obtain that $\varkappa_\nu = N\sigma_\nu$, i.e., effective cross section σ_ν is area of "opaque" (for frequency ν) disk, corresponding to one absorbing atom. In exactly this way it is possible to speak about effective cross section of atom or some other particle for scattering of quanta.

Bound-bound transitions are caused by quanta of strictly definite energy $h\nu$ lying within extraordinarily narrow bounds. This energy must correspond to difference between energies of two levels in atom. Therefore, we speak of such absorption as selective. Effective absorption cross sections of "isolated" atoms for these "chosen" quanta are extraordinarily great. For quanta of visible light they of order of 10^{-9} cm^2 in center of line (in middle of narrow interval of selective absorption.* Such cross sections correspond to very small mean free paths of quanta. For instance, for density $N \sim 10^{19}$ cm^{-3} (order of density of atmospheric air), mean free path would be on the order of $l = 1/\varkappa = 1/N\sigma \sim 10^{-10}$ cm.

Effective cross sections for bound-free absorption, i.e., for photoeffect, are much less, on order of $10^{-17} - 10^{-20}$ cm^2 ($l \sim \sim 10^{-2} - 10$ cm at $N \sim 10^{19}$ cm^{-3}). These magnitudes pertain, of course, only to quanta which, in general, are able to pull electron from atom, i.e., energy of which is higher than binding energy of electron.

In free-free transitions, for absorption of quantum it is necessary that electron fly at the time of absorption very close to

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*Effective absorption cross section in center of line having natural width, of the order λ^2, where λ is wave length of quantum. In scale of wave lengths natural width of lines in visible part of spectrum is on the order of 10^{-4}A = 10^{-12} cm (1 angstrom (A) is equal to 10^{-8} cm). Usually in gases width of lines are larger than natural, and cross section in center of line is accordingly less than λ^2. For greater detail see § 9 Chapter V.

ion — "collide" with ion (free electron is not able to absorb a quantum; it can only scatter it). Therefore, in this case, coefficient of so-called "braking" absorption is proportional to number of ions, as well as to number of free electrons in 1 cm^3: $\varkappa_{brak} \sim N_+ N_e$. It is possible to speak about effective cross section of ion $\sigma_{brak} = \varkappa_{brak}/N_+ \sim N_e$ only in a conditional sense, since this cross section is proportional to density of free electrons. It turns out, however, that in case of incomplete ionization, coefficient of "braking" absorption is proportional only to first power of density of gas, since to density is proportional the actual product $N_+ N_e$. For quanta which are the most common at a given temperature, coefficient of "braking absorption is approximately an order less than coefficient of bound-free absorption.

In case of tatal ionization, when in gas there are present only nuclei and electrons (and bound-free absorption in general does not occur), coefficient of "braking" absorption is proportional to square of density of gas.

Mainly free electrons scatter quanta* (if energy of quantum is great as compared to binding energy of electron in atom, then such an electron also can be considered as "free").

Quanta of not too high energies (much lower than self energy of electron: $m_e c^2 = 500$ ev, which are the only ones with which it is necessary to deal at ordinary temperatures, are scattered without change of energy. Effective scattering cross section is determined by calssical radius of electron r_0 and is equal to $\sigma_S = \frac{8}{3} \pi r_0^2 = 6.65 \cdot 10^{-25}$ cm^2 (this is so-called Thomson scattering cross section).

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*Let us note existence of effect of resonance scattering, in which bound electron absorbs quantum with transition into bound excited state and then emits it in an arbitrary direction. Effective cross section of resonance scattering in center of line, just as absorption cross section, is on the order of λ^2.

This cross section is very little; it corresponds to scattering mean free path $l_s \sim 10^5$ cm at density of electrons $N_e \sim 10^{19}$ cm^{-3}. During estimate of scattering length of large quanta, for which all electrons of atoms and molecules can be considered as free, by N_e we should understand the total number of electrons present in atoms. For instance, in air of normal density $N_{molec} = 2.67 \cdot 10^{19}$ cm^{-3}, and total number of electrons is 14.4 times as great. Scattering mean free path is equal to 37 m. It is necessary to note that effective cross section of very large, megaelectron-volt quanta differs from Thomson mean free path.

In incompletely ionized gas, scattering mean free path of quanta in continuous spectrum always is much larger than absorption mean free path. Only in completely ionized and very strongly rarefied gas, when "braking" absorption, which is proportional to N^2, becomes small, is scattering important.

Under "terrestrial" conditions light scattering practically always can be disregarded as compared to absorption.* Therefore, subsequently we will omit index "a" for quantities $\varkappa_\nu$, l_ν; we will mean by them coefficient of absorption and absorption mean free path.

Here we will complete general survey of mechanisms of interaction of radiation with substance. To detailed account of these problems will be dedicated Chapter V. Here nowhere will there be needed by us specific expressions for coefficients of absorption.

§ 3. Equilibrium Radiation and Ideal Black Body

Let us imagine an unbounded medium which is in a state of thermodynamic equilibrium at constant temperature T. Under steady-state

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*Under astrophysical conditions scattering sometimes is even greater than absorption.

conditions field of radiation is also equilibrium. Thermodynamic equilibrium of radiation is characterized by the fact that number of quanta or quantity of radiant energy emitted by substance in 1 sec in 1 cm^3 in given interval of frequencies $d\nu$ and in given interval of directions $d\Omega$ is exactly equal to number of absorbed quanta or quantity of radiant energy absorbed by substance in the same intervals $d\nu$, $d\Omega$. Field of equilibrium radiation is isotropic, i.e., does not depend on direction and does not depend on specific properties of medium, but is a universal function of frequency and temperature.

Spectral density function of equilibrium radiation $U_{\nu p}$ was derived by Planck at the dawn of development of quantum theory. It can be obtained by the most natural means with help of quantum statistics, which is obeyed by a "photon gas" (see, for instance, [4]). Quantity of energy of equilibrium radiation of frequency ν in 1 cm^3, taken over unit interval of frequencies is equal to

$$U_{\nu p}=\frac{8\pi h\nu^3}{c^3}\frac{1}{e^{\frac{h\nu}{kT}}-1}. \tag{2.10}$$

In virtue of isotropy, spectral intensity of equilibrium radiation is equal to

$$I_{\nu p}=\frac{cU_{\nu p}}{4\pi}=\frac{2h\nu^3}{c^2}\frac{1}{e^{\frac{h\nu}{kT}}-1}.^* \tag{2.11}$$

Distribution of energy of equilibrium radiation over frequencies which is given by Planck function (2.10) is depicted in Fig. 2.3 Maximum of this distribution lies at energy of quanta $h\nu_{max} = 2.822$ kT. With increase of temperature maximum is displaced in the direction of higher frequencies. In region of low frequencies $h\nu \ll kT$ formula of

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*In astrophysical literature instead of $I_{\nu p}$ there usually is used designation B_ν.

Planck reduces to classical formula of Rayleigh-Jeans:

$$U_{\nu p}=\frac{8\pi kT}{c^3}\nu^2,\quad h\nu\ll kT. \tag{2.12}$$

In region of large frequencies $h\nu \gg kT$ we obtain formula of Wien:

$$U_{\nu p}=\frac{8\pi h\nu^3}{c^3}e^{-\frac{h\nu}{kT}},\quad h\nu\gg kT. \tag{2.13}$$

Total density of equilibrium radiation is obtained by integration over frequencies from zero to ∞ of spectral density (2.10). Calculation gives the known expression:

$$U_p=\int_0^\infty U_{\nu p}\,d\nu=\frac{4\sigma T^4}{c}, \tag{2.14}$$

where $\sigma = 2\pi^5k^4/15h^3c^2 = 5.67\cdot10^{-5}$ erg/cm^2·sec·deg^4 is Stefan-Boltzmann constant ($U_p = 7.55\cdot10^{-15}\ T^{o4}$erg/cm^3).

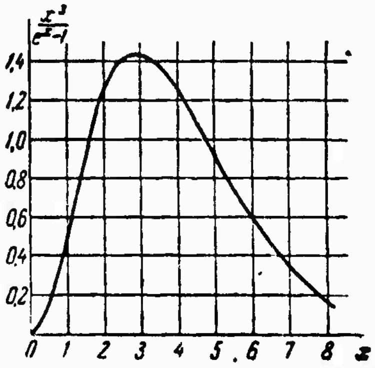

Fig. 2.3. Planck function $x^3(e^x - 1)^{-1}$, where $x = h\nu/kT$.

Proportionality of total density of equilibrium radiation to fourth power of temperature follows directly from second law of thermodynamics and the theorem known from classical electrodynamics that pressure of isotropic field of radiation is equal to one third of energy density: $p_\nu = U_p/3$. Substituting this expression in general thermodynamic relation $T\,dS = d\varepsilon + p\,dV$,* whereby specific energy we mean product of radiation density and volume $\varepsilon = U_pV$, and noticing that dS is total differential, we will obtain $U = \text{const}\ T^4$. We should mention that relation $p_\nu = U_p/3$ indicates that equilibrium radiation can be

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*Here S is entropy of radiation.

considered from thermodynamic point of view as ideal gas with adiabatic index $\gamma = 3/4$.

Inasmuch as field of equilibrium radiation is isotropic, radiation flux at any point of body is equal to zero. This means that if we (mentally) place in the body a plane surface, then unidirectional radiation fluxes through surface from the right to the left and from the left to the right will be exactly equal to each other in absolute value and opposite in direction. The magnitude of unidirectional flux itself, i.e., quantity of radiant energy flowing, let us say, from the left to the right in 1 sec through unit area will be obtained by putting in formula (2.2) the expression (2.11) for equilibrium intensity and integrating not over the entire solid angle, but only over a hemisphere. Unidirectional spectral flux is equal to

$$S_{\nu p} = \frac{cU_{\nu p}}{4} = \frac{2\pi h\nu^3}{c^2} \frac{1}{e^{\frac{h\nu}{kT}} - 1}. \tag{2.15}$$

Unidirectional flux integrated over spectrum is

$$S_p = \int_0^\infty S_{\nu p} d\nu = \frac{cU_p}{4} = \sigma T^4. \tag{2.16}$$

Let us imagine a body with constant temperature T, in which there is a cavity filled with equilibrium radiation. On 1 cm^2 of surface of the substance in 1 sec from the cavity there falls radiation flux $S_{\nu p}$. This flux, in general, is partially reflected from wall of cavity, and partially passes inside and is absorbed by the substance (we will assume that it does not pass clear through the body — the body is not bounded). Let us designate reflectivity by R_ν. and absorptivety of substance by A_ν; $A_\nu = 1 - R_\nu$. Quantity of radiation passing from cavity to the inside of the body and absorbed in the substance is equal to $S_{\nu p} \cdot A_\nu$. In virtue of equilibrium, the same quantity of radiation J'_ν is emitted in 1 sec from 1 cm^2 of surface of body in the direction of the cavity, i.e., $J'_\nu = S_{\nu p} \cdot A_\nu$. Absorptivity, reflectivity, magnitude of emission from surface are characteristics of body and state of substance; however, the ratio:

$$\frac{J'_\nu}{A_\nu} = S_{\nu p} = \frac{2\pi h\nu^3}{c^2} \frac{1}{e^{h\nu/kT} - 1} \tag{2.17}$$

does not depend on specific properties of body and is a universal function of frequency and temperature. This statement is called the Kirchhoff law.

Body, which completely absorbs all radiation incident on it is called ideal black body. For an ideal black body, by definition, $R_\nu = 0$, $A_\nu = 1$. From formula (2.17) it follows that from its surface there emerges a spectral flux equal to $S_{\nu p}$; integral over spectrum of flux is equal to $S_p = \sigma T^4$.

We will consider an unbounded solid medium with constant temperature T, in which radiation is in equilibrium with substance, and again will divide it by an imaginary plane surface. Unidirectional fluxes through surface are equal to $S_{\nu p}$. Quanta which intersect surface from the left to the right are "generated" on the left of the surface, and those going from the right to the left are generated on the right of the surface. Let us mentally remove the substance from one side of the surface, let us say, from the right, assuming thus that temperature of substance on the left is not changed. Furthermore, we will assume that the medium possesses index of refraction equal to one, just as the vacuum which will be formed on the right, i.e., the boundary does not reflect light. Then, after "removal" of substance from the right, quanta do not arrive at all from the vacuum side, and flux of quanta from the left to the right from the substance obviously will not be changed and will be as before equal to $S_{\nu p}$. Thus, the plane half-space filled with substance with index of refraction equal to one and constant temperature T sends from the surface radiation flux $S_{\nu p}$; i.e., it radiates as an ideal black body with temperature T.

§ 4. Stimulated Emission

We will consider balance of absorption and emission of light in substance located in field of radiation I_ν. Quantity of radiant energy in interval of frequencies $d\nu$ and interval of directions $d\Omega$, absorbed in 1 cm^3 in 1 sec is equal to

$$I_\nu d\nu d\Omega \varkappa_\nu = \text{absorption per 1 sec per 1 cm}^3. \quad (2.18)$$

Quantity of energy spontaneously emitted by substance per 1 cm^3 per 1 sec in the same interval $d\nu$ $d\Omega$; is equal to

$$j_\nu d\nu d\Omega = \text{spontaneous emission per 1 sec per 1 cm}^3.$$

Quantity of spontaneous emission (radiation factor j_ν) is determined only by properties of substance and its state: kind of atoms, temperature, on which degree of excitation of atoms depends, etc., and absolutely does not depend on whether there is radiation in space or not. This, however, does not exhaust the total quantity of radiation emitted by substance.

There exists so-called stimulated or induced emission. Probability of stimulated emission of a quantum of given frequency and given direction is proportional to intensity of radiation of the same frequency and the same direction at given point of space. The existing quanta promote transitions of excited atomic systems accompanied by emission of the very same quanta. In quantum theory it appears that total emission probability of given quanta is proportional to the quantity

1 + n, where n is number of pl h definite direction of polarization located in the same phas into which the emitted quantum enters. This number is equal to $n = c^2I_\nu/2h\nu^3$.* Thus, total quantity of radiation emitted in 1 sec in 1 cm^3 in interval $d\nu\, d\Omega$, is equal to

$$j_\nu d\nu d\Omega\left(1+\frac{c^2}{2h\nu^3}I_\nu\right) = \text{total emission in 1 sec in 1 cm}^3. \qquad (2.19)$$

First term in parentheses corresponds to spontaneous emission, and the second — to stimulated emission.

In state of thermodynamic equilibrium, emission and absorption of quanta of given frequency and direction exactly compensate one another, so that expressions (2.18) and (2.19) should be equated, where intensity of radiation I_ν is replaced by the equilibrium quantity $I_{\nu p}$.

Taking into account formula (2.11) for equilibrium intensity, we will find that ratio of emittance of any substance to its absorptivity is a universal function of frequency and temperature:

$$\frac{j_\nu}{\varkappa_\nu} = \frac{I_{\nu p}}{1+\frac{c^2}{2h\nu^3}I_{\nu p}} = \frac{2h\nu^3}{c^2}e^{-\frac{h\nu}{kT}}. \qquad (2.20)$$

This relationship constitutes one of forms of Kirchhoff law.

Formula (2.20) can be conveniently rewritten in the form

$$j_\nu = I_{\nu p}\varkappa_\nu\left(1-e^{-\frac{h\nu}{kT}}\right). \qquad (2.21)$$

Emittance in all directions is equal to

$$J_\nu = 4\pi j_\nu = cU_{\nu p}\varkappa_\nu\left(1-e^{-\frac{h\nu}{kT}}\right). \qquad (2.22)$$

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*Phase volume corresponding to element $d\nu\, d\Omega\, d\mathbf{r}$, in which there are located $f\, d\nu\, d\Omega\, d\mathbf{r}$ quanta, is $dp\, d\mathbf{r}$, where dp is element of volume in momentum space. Inasmuch as momentum of quantum is equal to $p = h\nu\Omega/c$, $dp = p^2\, dp\, d\Omega = h^3\nu^2\, d\nu\, d\Omega/c^3$. Number of phase cells in element of phase space $dp\, d\mathbf{r}$ is equal to $dp\, d\mathbf{r}/h^3$, and consequently, number of photons in one cell is equal to $f\, d\nu\, d\Omega\, d\mathbf{r}\, h^3 dp\, d\mathbf{r} = c^2f/\nu^2 = c^2I_\nu/h\nu^3$. Number of photons with definite direction of polarization is equal to half of this number, i.e., $c^2I_\nu/2h\nu^3$.

Kirchhoff law constitutes expression of general principle of detailed balance in reference to processes of emission and absorption of light. It permits calculation of emittance of substance, if there is known its coefficient of absorption (and conversely).

Existence of processes of stimulated emission, i.e., transitions of excited atom whose probability depends on number of "particles" (photons) already existing in final state of atom plus photon system is characteristic for processes with participation of photons ("particles") obeying quantum statistics of Bose. Namely, due to existence of such processes, distribution function of photon gas differs from distribution function of gas obeying classical statistics of Boltzmann, where number of particles with energy ε is proportional to $e^{-\varepsilon/kT}$, and not $(e^{\varepsilon/kT} - 1)^{-1}$, as for photons ($\varepsilon = h\nu$).

In order to explain this, we will consider the simplest case, when atom possesses two energy levels, ε_1 and ε_2 ($\varepsilon_2 > \varepsilon_1$), and transition from upper energy state to lower is accompanied by emission of quantum $h\nu = \varepsilon_2 - \varepsilon_1$, and transition from lower to upper is accompanied by absorption of quantum $h\nu$. Probability of absorption, i.e., $\varkappa_\nu$, is proportional to number of atoms in lower energy state, which, according to the law of Boltzmann, is proportional to $e^{-\varepsilon_1/kT}$. Probability of spontaneous emission j_ν is proportional to number of atoms in upper energy state, i.e., $e^{-\varepsilon_2/kT}$

We will assume that stimulated emission does not exist. Then in equilibrium the number of events of spontaneous emission of quanta $h\nu$ would be equal to number of events of absorption, i.e., instead of formulas (2.20) or (2.21), we would have equalities

$$\frac{j_\nu}{\varkappa_\nu} = I_{\nu p}, \quad j_\nu = I_{\nu p}\varkappa_\nu, \tag{2.23}$$

but $j_\nu \sim e^{-\varepsilon_2/kT}$, $\varkappa_\nu \sim e^{-\varepsilon_1/kT}$, so that

$$\frac{j_\nu}{\varkappa_\nu} = I_{\nu p} = \text{const}\, e^{-\frac{\varepsilon_2-\varepsilon_1}{kT}} = \text{const}\, e^{-\frac{h\nu}{kT}}.$$

In other words, for intensity of equilibrium radiation, or which is the same, for distribution function of quanta, we would obtain law of Boltzmann, just as for "usual" particles. In fact, law of Boltzmann is valid only for large quanta $h\nu \gg kT$ in the Wien region.

Only taking into account processes of stimulated emission, consideration of balance of emission and absorption of quanta leads to formula of Planck for distribution function of photons. In our example of an atom with two energy levels, we will thus obtain

$$\frac{j_\nu}{\varkappa_\nu} = \frac{I_{\nu p}}{1+\frac{c^2 I_{\nu p}}{2h\nu^3}} = \text{const}\, e^{-\frac{\varepsilon_2-\varepsilon_1}{kT}} = \text{const}\, e^{-\frac{h\nu}{kT}},$$

whence there follows the formula of Planck for intensity $I_{\nu p}$ (for const = $\frac{2h\nu^3}{c^2}$).

From conducted reasoning it follows that role of stimulated emission as compared to spontaneous under conditions of equilibrium tends to zero as $h\nu/kT \to \infty$, i.e., in Wien region of spectrum. This we may see directly from formula (2.19), if we consider that during equilibrium in the limit $h\nu/kT \to \infty$.

$$I_\nu = I_{\nu p} \sim e^{-\frac{h\nu}{kT}} \to 0.$$

Conversely, in Rayleigh – Jeans region of spectrum, where $h\nu \ll kT$, relative role of stimulated emission is great: in formula (2.19)

$$1+\frac{c^2}{2h\nu^3} I_{\nu p} = 1 + \frac{1}{e^{\frac{h\nu}{kT}}-1} \approx 1 + \frac{kT}{h\nu},$$

so that ratio of probabilities of stimulated and spontaneous emissions is equal to $kT/h\nu \gg 1$.

It is necessary to note that in case when field of radiation is non-equilibrium, presented considerations about comparative role of spontaneous and forced emissions in general are incorrect, since stimulated emission is proportional to actual intensity of radiation, which in absence of equilibrium can be arbitrary.

§ 5. Equation of Radiation Transfer

We will form kinetic equation for distribution function of quanta of given frequency. Inasmuch as this function with accuracy up to the constant factor $h\nu c$ coincides with intensity of radiation, it is possible to write equation directly for intensity. In such form, kinetic equation is usually called equation of radiation transfer.

We will be interested in radiation of frequency ν in unit interval of frequencies which propagates inside unit solid angle in definite direction $\mathbf{\Omega}$. Let us consider balance of radiation in elementary cylinder with area of base $d\sigma$ and height ds, which is located at given point of space in such a way that direction $\mathbf{\Omega}$ coincides with generatrix of cylinder and is perpendicular to its bases (Fig. 2.4). During the time dt into left base flows quantity of radiation $I_\nu(\mathbf{\Omega}, \mathbf{r}, t)\, d\sigma\, dt$. From right base during the same interval of time dt there flows quantity of radiation $(I_\nu + dI_\nu)\, d\sigma\, dt$.

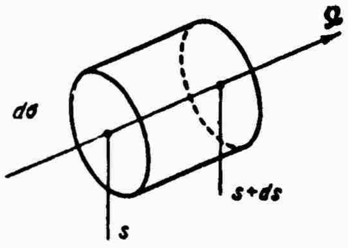

Fig. 2.4. For derivation of equation of radiation transfer.

Intensity I_ν is function of coordinates and time. Increase of intensity of beam of light during passage from left base to right base is composed of the local increase during the time of passage by light over path ds and of the increase during passage from coordinate s to coordinate $s + ds$ at given moment of time

$$dI_\nu = \frac{\partial I_\nu}{\partial t}\frac{ds}{c} + \frac{\partial I_\nu}{\partial s}ds.$$

Change of intensity of beam occurs due to emission and absorption of light with considered characteristics in our cylinder. (In accordance with remark made at the end of § 2, light scattering will be disregarded). Quantity of radiation emitted in cylinder during the time dt, according to formula (2.19), is equal to

$$j_\nu\left(1+\frac{c^2}{2h\nu^3}I_\nu\right)d\sigma\,ds\,dt.$$

There is absorbed in it in the same time the quantity of radiation $\varkappa_\nu I_\nu$ dσ ds dt. By forming balance and dividing obtained expression by product of differentials dσ ds dt, we will obtain equation

$$\frac{1}{c}\left(\frac{\partial I_\nu}{\partial t}+c\Omega\nabla I_\nu\right)=j_\nu\left(1+\frac{c^2}{2h\nu^3}I_\nu\right)-\varkappa_\nu I_\nu. \qquad (2.24)$$

We here replaced in left side partial derivative along direction $\partial I_\nu/\partial s$ by equivalent vector expression $\Omega\nabla I_\nu$.

Combination in parentheses in left side constitutes simply the "particle" derivative of intensity with respect to time, i.e., time derivative of intensity of given packet of quanta (cf. with equation of motion in hydrodynamics (1.6)).

We will transform right side of equation (2.24) by combining terms, corresponding to absorption and stimulated emission, inasmuch as they both are proportional to unknown function of coordinates and time — to intensity of radiation. Let us moreover introduce into factor before I_ν in term of stimulated emission in place of radiation factor j_ν its expression in terms of coefficient of absorption (2.21), into which we will substitute formula (2.11) for equilibrium intensity. Right side of equation will take form

$$j_\nu-\varkappa_\nu\left(1-e^{-\frac{h\nu}{kT}}\right)I_\nu. \qquad (2.25)$$

Hence it is clear that stimulated emission can be treated as some decrease of absorption: part of quanta absorbed here also are emitted again with the same frequency and in the same direction, and probability of this "re-emission" is equal to $e^{-h\nu/kT}$. Physically such acts of "re-emission" in no way are apparent, and it is possible in general to exclude them from consideration, if it is considered that coefficient of absorption has somewhat smaller magnitude:

$$\varkappa'_\nu = \varkappa_\nu \left(1 - e^{-\frac{h\nu}{kT}}\right). \qquad (2.26)$$

Interaction of radiation with substance can be represented as if there exists only spontaneous emission and effective absorption described by coefficient $\varkappa'_\nu$, corrected for stimulated emission.

In new treatment Kirchhoff law (2.21) obtains form

$$j_\nu = \varkappa'_\nu I_{\nu p}, \quad \varkappa'_\nu = \varkappa_\nu \left(1 - e^{-\frac{h\nu}{kT}}\right). \qquad (2.27)$$

Introducing this expression into the right side of equation of transfer (2.24), we will write equation in following, final form:

$$\frac{1}{c}\frac{\partial I_\nu}{\partial t} + \Omega \nabla I_\nu = \varkappa'_\nu (I_{\nu p} - I_\nu). \qquad (2.28)$$

We integrate equation (2.28) over all directions Ω (over solid angle). Remembering definitions of density and flux of radiation (2.1), (2.2), we will obtain

$$\frac{\partial U_\nu}{\partial t} + \operatorname{div} S_\nu = c\varkappa'_\nu (U_{\nu p} - U_\nu). \qquad (2.29)$$

This equation can be considered as equation of continuity for radiation of given frequency. It expresses law of conservation of energy of radiation and is fully analogous to equation of energy in hydrodynamics written in "divergent" form (1.10).

Equation of transfer of radiation (2.28) is a partial differential equation with respect to intensity as a function of coordinates, time, and direction of $I_\nu(r, t, \Omega)$ and describes field of non-equilibrium radiation. Usually thermodynamic equilibrium in the actual substance is established very rapidly, so that substance can be considered to be thermodynamically equilibrium at every point of space and at every moment of time. State of substance thus is characterized by two parameters, for instance temperature and density. Equation of transfer of radiation contains quantities depending on kind and state of substance: coefficient of absorption $\varkappa'_\nu$, which depends on properties of substance, its temperature and density, and equilibrium intensity $I_{\nu p}$ which is a function only of temperature.

Equation (2.28) describes, in particular, process of establishment of equilibrium of radiation with substance in time.

Let us imagine an unbounded medium with constant density which is initially cold, so that radiation is lacking. Let us assume that at initial moment t = 0 substance is "instantaneously" heated to constant temperature T, which then is maintained constant in time. Let us see how intensity of radiation changes in time. Obviously, space gradients in this case are equal to zero, $\varkappa'_\nu$ = const, $I_{\nu p}$ = const. Solution of equation (2.28) in this case has the form

$$I_\nu(t) = I_{\nu p}(1 - e^{-c\varkappa'_\nu t}), \tag{2.30}$$

i.e., intensity of radiation asymptotically tends to equilibrium, and relaxation time for establishment of equilibrium of radiation with substance is equal to $t_p = 1/c\varkappa'_\nu = l'_\nu/c = l_\nu/(1 - e^{-h\nu/kT})\,c$. For instance, at $l_\nu = 1$ cm at maximum of Planck spectrum $h\nu = 2.8$ kT, $t_p = 3\cdot10^{-11}$ sec.

§ 6. Integral Expressions for Intensity of Radiation

We will find formal solution of equation of transfer of radiation, considering quantities depending only on state of substance $I_{\nu p}(T)$,

$\varkappa'_\nu(T,\rho)$, as known functions of coordinates and time. Let us consider at first for simplicity the steady-state case, when distributions of temperature and density, and also the field of radiation do not depend on time. We will be interested in radiation at point **r** of body with direction of propagation Ω (Fig. 2.5). Let us draw a ray through given point in given direction and designate coordinate along ray by s. Noticing that differential expression in left side of equation of transfer (2.28) is the total derivative of intensity of a given packet of quanta along ray of their propagation, we will rewrite equation in the form

$$\frac{dI_\nu}{ds} + \varkappa'_\nu I_\nu = \varkappa'_\nu I_{\nu p}. \qquad (2.31)$$

This equation can be considered as ordinary linear equation with respect to intensity along the ray. Solution of it is

$$I_\nu(s) = \int_{s_0}^{s} \varkappa'_\nu I_{\nu p} \exp\left[-\int_{s'}^{s} \varkappa'_\nu ds''\right] ds' + I_{\nu_0} \exp\left[-\int_{s_0}^{s} \varkappa'_\nu ds''\right]. \qquad (2.32)$$

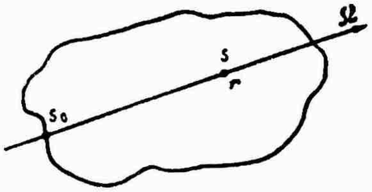

Fig. 2.5. Diagram explaining limits of integration in formula (2.32).

Here $I_\nu(s)$ is intensity $I_\nu(\mathbf{r}, \Omega)$, which is considered as function of coordinate s along ray. Integration over ray is conducted in general from "$-\infty$," and actually from boundary of body s_0 (as shown in Fig. 2.5). By $I_{\nu 0}$ is designated constant of integration.

Let us clarify physical meaning of obtained solution.

Radiation flowing per unit time through element of unit cross section at point s of the ray (per unit of solid angle) is composed of all quanta generated in tube of unit cross section along the ray. At point s' on segment of ray ds' there is generated a quantity of radiation $j_\nu\, ds' = \varkappa'_\nu I_{\nu p}\, ds'$, which propagates along ray Ω in unit solid angle.

From point s' to point s there reaches only a fraction exp $[-\int_{s'}^{s} \varkappa'_\nu \, ds'']$ of this radiation; the rest is absorbed along the path. Total intensity is composed of quanta generated on all elementary segments ds', i.e., is equal to integral over the ray. If radiating body has finite dimensions, then it is necessary to integrate actually from boundary of body s_0 to point s. Thus, there is obtained first term in (2.32). Second term is radiation entering body on boundary s_0 from without, from some external, outside sources. Constant of integration $I_{\nu 0}$ is intensity of this radiation entering the body. Factor exp $[-\int_{s'}^{s} \varkappa'_\nu \, ds'']$ takes into account its attenuation along path from s_0 to s due to absorption. Coefficient of absorption $\varkappa'_\nu$ and equilibrium intensity $I_{\nu p}$ depend on point along ray due to dependence on temperature and density of substance, which in some way are distributed along the ray. If these functions are known, then finding of intensity at any point of the body reduces, as one may see from formula (2.33), simply to quadrature — integration along the ray.

We will generalize solution (2.33) to the non-steady-state case, when temperature and density, and consequently $I_{\nu p}$, $\varkappa'_\nu$ and unknown intensity I_ν depend on time. Obviously, by moment t to point s there arrive from point s' quanta generated at earlier moment of time $t - \frac{s - s'}{c}$. In exactly the same way, on their path they are absorbed by substance at point s" in accordance with value of coefficient of absorption at the time of passage through this point $t - \frac{s - s''}{c}$. Therefore, non-steady-state solution of equation of transfer can be written in the form

$$I_\nu(s, t) = \int_{s_0}^{s} (\varkappa'_\nu I_{\nu p})_{s', t-\frac{s-s'}{c}} \exp\left[-\int_{s'}^{s} (\varkappa'_\nu)_{s'', t-\frac{s-s''}{c}} ds''\right] ds' + \qquad (2.33)$$

$$+ (I_{\nu 0})_{s_0, t-\frac{s-s_0}{c}} \exp\left[-\int_{s_0}^{s} (\varkappa'_\nu)_{s'', t-\frac{s-s''}{c}} ds''\right].$$

where actual value of boundary coordinate s_0 is taken at the time $t - \frac{s - s_0}{c}$. It is easy to verify by direct substitution that expression (2.33) indeed satisfies non-steady-state equation of transfer. From formulas (2.32) or (2.33) it is clear that contribution of distant sources in strongly absorbing medium to intensity at given point exponentially decreases with increase of distance. To point s there reach quanta generated only in the nearest neighborhood of point at distances not greater than several radiation mean free paths, or more exactly, at optical distances of not more than several units. This assertion becomes especially graphic if coefficient of absorption is constant along the ray. Then exponential factors acquire the form

$$\exp\left[-\int_{s'}^{s} \varkappa'_\nu \, ds''\right] = \exp\left[-\varkappa'_\nu (s - s')\right] = \exp\left[-\frac{s - s'}{l'_\nu}\right]; \quad l'_\nu = \frac{1}{\varkappa'_\nu}.$$

The only exception, in principle, is the case of extraordinarily sharp change of temperature, when increase of emittance $j_\nu = \varkappa'_\nu I_{\nu p}$ with distance from point has a stronger effect than absorption along the path with increase of distance passed over. However, in practice this almost never happens, and main contribution to integrals (2.32), (2.33) is given by segment of ray near considered point with magnitude on the order of several (two-three) radiation mean free paths. But light passes over such a distance in a very small time l'_ν/c, which, as a rule, is considerably less than characteristic times during which there occurs noticeable change of state of substance (temperature and density); for instance, for mean free path of $l'_\nu = 3$ cm time $l'_\nu/c \approx 10^{-10}$ sec. It is much less than characteristic times with which it is necessary to deal in usual hydrodynamic flows. This is connected with the fact that usually speed of substance is much less than velocity of light.

The noted circumstance is very significant. It means that practically in all cases the field of radiation at every moment of time can be considered as quasi-steady-state, corresponding to instantaneous distribution of sources of emission and absorption, i.e., distribution of temperature and density of substance.

In equation of transfer of radiation, consequently, it is possible to omit derivative of intensity with respect to time and to consider time as a parameter on which temperature and density of substance depend, i.e., $I_{\nu p}$ and $\varkappa'_\nu$. Subsequently we will always start with such a simplified equation of transfer

$$\Omega\nabla I_\nu = \varkappa'_\nu (I_{\nu p} - I_\nu) \qquad (2.34)$$

or its solution in form (2.32).

§ 7. Radiation of a Plane Layer

In general, transfer of radiation and radiant heat exchange affect state of substance, its motion or distribution of temperature in steady state. This influence is connected with the fact that when emitting and absorbing light, substance loses or obtains energy, is cooled or heated. In general, state of substance is described by equations of hydrodynamics, which in the presence of radiant heat exchange should be generalized taking into account interaction of radiation with substance. Inasmuch as radiation transfer itself depends on state of substance, its temperature and density, then, in general, system of equations describing substance and radiation consists of equations of hydrodynamics generalized in the appropriate way and equation of radiation transfer.

In many cases, however, "reverse" influence of radiation on state of substance is small, or can be considered by any approximate method. For instance, at sufficiently low temperatures radiant heat exchange or loss of energy of body due to radiation are insignificant. Thus the state of substance practically does not depend on radiation, and problems of finding radiation field and description of state of substance are separated. State of substance is described, for instance, by equations of hydrodynamics, and field of radiation can be found at every moment on the basis of known distributions of temperature and density and known coefficients of absorption.

As a rule, practical interest in this case is presented by determination of not the entire field of radiation in medium (inasmuch as it all the same does not affect state of medium), but finding of radiation going out from surface of body, i.e., the question about incondescence of a heated body, about brightness of its surface, spectrum of radiation, flux distribution by angles, etc.

If there are known optical properties of substance, i.e., coefficient of absorption $\varkappa_\nu'$* as function of frequency, temperature, and density and distributions of temperature and density in the body, then the answer to all these questions is contained in integral formula for intensity (2.32).

If we are interested in radiation going out from surface of body, it is possible, without disturbing generality, to measure coordinate along ray s from surface into depth of body and to extend integration along the ray to infinity:

$$I_\nu(\Omega)=\int_0^\infty I_{\nu p}[T(s)]\,e^{-\int_0^s \varkappa_\nu' ds'}\varkappa_\nu'(s)\,ds. \qquad (2.35)$$

---

*We recall that we consider here only media with index of refraction equal to one, which are gasses.

If body is bounded, then outside of its boundaries coefficient of absorption is equal to zero and corresponding segment of integration drops out. If body is bounded, but from without from the "rear" side into it there penetrates a radiation flux, then by extending integration over the ray to infinity we thereby include in the integral these "outside" sources of light.

Let us consider several simple examples having practical interest. Let us assume that body occupies infinite half-space $x > 0$ and is bounded by a plane surface. Temperature of body is constant; coefficient of absorption can change arbitrarily from point to point (but in such a manner that optical thickness of body $\int_0^\infty \varkappa'_\nu\, dx$ is infinite).

In this case intensity of radiation at the surface of body is equal simply to $I_{\nu p}(T)$, since

$$I_\nu(\Omega) = \int_0^\infty I_{\nu p} e^{-\tau} d\tau = I_{\nu p}; \quad d\tau = \varkappa'_\nu\, ds, \quad \tau = \int_0^s \varkappa'_\nu\, ds.$$

Body radiates as an ideal black body with temperature T.

Intensity I_ν is quantity of radiant energy passing in 1 sec in unit of solid angle through unit area placed perpendicularly to direction of motion of quanta.* For a black radiator it does not depend on angle. Quantity of radiant energy going out in 1 sec through 1 cm^2 of surface at angle ϑ to normal per unit of solid angle (we will call this quantity radiative capacity of body i_ν** is equal to

$$i_\nu = I_\nu(\vartheta)\cos\vartheta. \tag{2.36}$$

For a black radiator

$$i_\nu = I_{\nu p}\cos\vartheta. \tag{2.37}$$

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*Dimension of I_ν is energy/cm^2·sec·sterad·frequency = erg/cm^2 × × sterad.

**We should not confuse it with radiative capacity of a medium j_ν or J_ν.

Let us consider radiation of plane layer of finite thickness d with constant temperature T and coefficient of absorption $\varkappa'_\nu$.

Intensity of radiation at the surface in direction forming angle ϑ with normal (Fig. 2.6) is equal to

$$I_\nu(\vartheta) = \int_0^{d/\cos\vartheta} I_{\nu p} e^{-\frac{\varkappa'_\nu x}{\cos\vartheta}} \varkappa'_\nu \frac{dx}{\cos\vartheta} = \int_0^{\varkappa'_\nu d/\cos\vartheta} I_{\nu p} e^{-\frac{\tau_\nu}{\cos\vartheta}} \frac{d\tau_\nu}{\cos\vartheta} = \tag{2.38}$$

$$= I_{\nu p}\left(1 - e^{-\frac{\varkappa'_\nu d}{\cos\vartheta}}\right) = I_{\nu p}\left(1 - e^{-\frac{\tau_\nu}{\cos\vartheta}}\right),$$

where $\tau_\nu = \int_0^d \varkappa'_\nu \, dx$ is optical thickness of layer in direction of normal to surface.

From formula (2.38) it is clear that intensity of radiation of layer of finite thickness is always smaller than equilibrium intensity. Spectrum differs from Planck spectrum $I_{\nu p}(T)$ by the factor $1 - e^{-\tau_\nu/\cos\vartheta}$. This factor depends on frequency due to frequency dependence of coefficient of absorption. It tends to 1 only as $d \to \infty$. Most sharply is expressed the difference of intensity from Planck intensity in direction of normal to surface, in which segment of ray with sources is minimum (is equal to d). Spectrum tends to Planck spectrum at large angles to the normal, when $\vartheta \to \pi/2$, $\cos\vartheta \to 0$. In dependence upon thickness of layer d, greatest difference of the spectrum from Planck spectrum should be observed in the limit of an optically thin layer, i.e., at angles such that $\varkappa'_\nu d/\cos\vartheta \ll 1$.

Expanding in this case the exponential function, we will find with accuracy up to terms of the second order of smallness:

$$I_\nu = I_{\nu p} \frac{\varkappa'_\nu d}{\cos\vartheta} < I_{\nu p}. \tag{2.39}$$

Intensity at the surface is proportional to $1/\cos\vartheta$, and emissive power of layer thus does not depend on angle

$$i_\nu = I_\nu \cos\vartheta = I_{\nu p}\varkappa'_\nu d \text{ for } \cos\vartheta \gg \tau_\nu. \qquad (2.40)$$

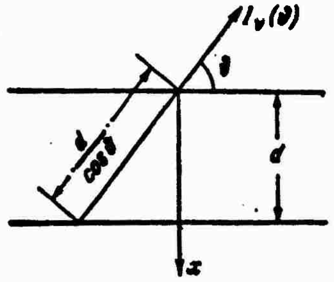

Fig. 2.6. Diagram for problem about radiation of plane layer.

It is necessary to note that the idea of "optical thinness" of layer depends on angle: there will always be found such large angles $\vartheta \approx \pi/2$, $\cos\vartheta \ll 1$, that the layer for these directions will be "optically thick," so that layer c $\tau_\nu \ll 1$ at large angles $\vartheta \approx \pi/2$ all the same radiates as a black body. At small angles, when $\tau_\nu/\cos\vartheta \ll 1$ and layer is optically thin, it emits as a volume radiator; quanta generated at any point emerge from layer practically without absorption along their paths. In the layer there is no "self-absorption" and every element of volume introduces an identical contribution into the radiation going out from the surface. This serves as the basis for the term "volume radiator." An optically thick body radiates "from its surface," since quanta, generated in the depth do not emerge from the body; they are absorbed along their path.

In many cases there presents interest not intensity of radiation at given angle, but radiation flux from surface of body, i.e., quantity of energy going out in 1 sec from 1 cm^2 of surface of body in all directions. This quantity is called brightness of surface (spectral or integral).

Spectral brightness of surface, obviously, is equal to

$$S_\nu = \int\limits_{\text{over hemisphere}} \cos\vartheta I_\nu(\Omega)\,d\Omega, \qquad (2.41)$$

where $I_\nu(\Omega)$ is given by formula (2.35), ϑ is angle between direction of propagation of radiation and normal to surface.

We will find brightness of surface of plane layer; thus we will consider temperature and coefficient of absorption as variables, but depending only on coordinate x (see Fig. 2.6). Let us replace in formula (2.35) ds by dx/cos ϑ and introduce optical thickness:

$$d\tau'_\nu = \varkappa'_\nu \, dx, \quad \tau'_\nu = \int_0^x \varkappa'_\nu \, dx. \tag{2.42}$$

Then

$$I_\nu(\vartheta) = \int_0^\infty I_{\nu p} e^{-\frac{\tau'_\nu}{\cos\vartheta}} \frac{d\tau'_\nu}{\cos\vartheta}, \quad \frac{\pi}{2} > \vartheta > 0. \tag{2.43}$$

Let us place this expression in (2.41) and integrate over angles ($d\Omega = 2\pi \sin\vartheta \, d\vartheta$):

$$S_\nu = 2\pi \int_0^{\pi/2} \cos\vartheta \sin\vartheta \, d\vartheta \int_0^\infty I_{\nu p} e^{-\frac{\tau'_\nu}{\cos\vartheta}} \frac{d\tau'_\nu}{\cos\vartheta} = 2\pi \int_0^\infty I_{\nu p} \, d\tau'_\nu \int_0^1 d(\cos\vartheta) \, e^{-\frac{\tau'_\nu}{\cos\vartheta}}.$$

Introducing variable w = 1/cos ϑ and taking into account the definition of the tabulated functions — exponential integral functions,

$$E_n(z) = \int_1^\infty e^{-zw} \frac{dw}{w^n}, \quad n = 1, 2 \ldots, \tag{2.44}$$

and also replacing equilibrium intensity by equilibrium radiation density by the formula $I_{\nu p} = cU_{\nu p}/4\pi$, we will obtain

$$S_\nu = \frac{c}{2} \int_0^\infty U_{\nu p}[T(\tau'_\nu)] \, E_2(\tau'_\nu) \, d\tau'_\nu \tag{2.45}$$

or for layer of finite optical thickness $\tau_\nu = \int_0^d \varkappa'_\nu \, dx$,

$$S_\nu = \frac{c}{2} \int_0^{\tau_\nu} U_{\nu p} E_2(\tau'_\nu) \, d\tau'_\nu. \tag{2.46}$$

Using known property of exponential integrals

$$\int_0^\infty E_2(z) \, dz = \frac{1}{2},$$

we will obtain for semi-infinite body of constant temperature

$$S_\nu = \frac{cU_{\nu p}}{4} = S_{\nu p}. \tag{2.47}$$

As we should have expected, spectral brightness is equal to brightness of ideal black body.

Brightness of layer of finite thickness and constant temperature is euqal to

$$S_\nu = \frac{cU_{\nu p}}{2}\int_0^{\tau_\nu} E_2(\tau'_\nu)\, d\tau'_\nu = \frac{cU_{\nu p}}{4}[1-2E_3(\tau_\nu)] = S_{\nu p}[1-2E_3(\tau_\nu)]. \tag{2.48}$$

It is always less than brightness of ideal black body of the same temperature and tends to the latter as $\tau_\nu \to \infty$.

For optically thin layer

$$\begin{gathered}\tau_\nu < 1, \quad E_2(\tau'_\nu) \approx E_2(0) = 1, \\ 2E_3(\tau_\nu) \approx 1 - 2\tau_\nu\end{gathered} \tag{2.49}$$

and

$$S_\nu = \frac{cU_{\nu p}}{2}\tau_\nu = S_{\nu p}\cdot 2\tau_\nu, \quad 2\tau_\nu \ll 1. \tag{2.50}$$

§ 8. Effective or Luminance Temperature of Surface of a Nonuniformly Heated Body

Spectral brightness of surface of a nonuniformly heated body is very conveniently characterized by effective or luminance temperature $T_{\nu ef}$. By the latter is understood temperature of ideal black body sending from its surface in given section of spectrum precisely the same radiation flux as the considered real body.

By comparing formulas (2.46) and (2.47), we will obtain expression determining effective temperature in the plane case:

$$U_{\nu p}(T_{\nu ef}) = 2\int_0^{\tau_\nu} U_{\nu p}[T(\tau'_\nu)]\, E_2(\tau'_\nu)\, d\tau'_\nu, \tag{2.51}$$

or, substituting Planck function for $U_{\nu p}$,

$$\frac{1}{e^{\frac{h\nu}{kT_{\nu ef}}}-1} = 2\int_0^{\tau_\nu} \frac{1}{e^{\frac{h\nu}{kT}}-1} E_2(\tau'_\nu)\, d\tau'_\nu. \tag{2.52}$$

Effective temperature depends on frequency. Only in case of ideal black body is it identical for all frequencies and equal to temperature of substance.

It is possible to introduce effective temperature of integrated radiation of body over the spectrum, according to the definition

$$S=\sigma T_{\text{эф}}^4, \tag{2.53}$$

where S is integrated flux going out from surface of body. Obviously, effective temperature of integrated radiation is a certain average magnitude with respect to spectral effective temperatures.

We will see what the connection is between spectrum of radiation of body and frequency dependence of coefficient of absorption.

We will consider optically thick body; radius of curvature of surface, let us assume, will be large as compared to mean free paths of radiation, so that body can be considered as flat. Let us assume that temperature falls toward the surface, as depicted in Fig. 2.7.

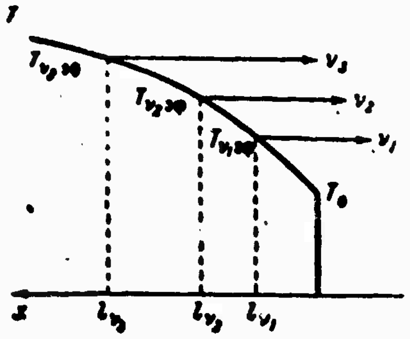

Fig. 2.7. Concerning the question about radiation of body with temperature falling toward the surface.

Radiation flux of frequency ν going out from surface is determined by integral over sources (2.45). Due to self-absorption, which is taken into account by fast dropping with τ_ν' of exponential integral, main contribution to integral is given by layer on the order of mean free path l_ν' near surface (with optical thickness $\tau_\nu^{\prime 1}$ on the order of unity). In other words, quanta going out from surface of body are generated mainly in layer near surface with optical thickness on the order of unity (more exactly, two-three units). This shell may be called radiating. Quanta generated in deeper layers are practically completely absorbed before getting out of body. Effective temperature, as follows from formula (2.52), is equal to certain average temperature of radiating layer.

Quanta going out from surface which have those frequencies for which absorption is stronger, and mean free path is less are radiated in layers closer to surface and less heated. Conversely, more weakly absorbed frequencies emerge from deeper and more heated layers. Thus, if temperature of substance falls toward surface (as this usually occurs), effective temperature of more strongly absorbed frequencies is less than for more weakly absorbed ones. This is schematically depicted in Fig. 2.7, on which arrows shown "place" from which quanta of different frequencies are radiated. "Places" are tentatively referred to distances from surface equal to mean free path of quanta.

Spectrum of radiation of nonuniformly heated body differs from Planck spectrum — more, the stronger the frequency and temperature dependence of coefficient of absorption, and the steeper the curve of temperature near surface at distances on the order of mean free paths of quanta.

In Fig. 2.8 there is schematically depicted spectrum of radiation of body with temperature falling toward surface and inverse dependence of coefficient of absorption on frequency, with which low frequencies are absorbed more strongly than high frequencies.

On the continuous spectrum there are drawn discrete lines corresponding to bound-bound transitions in atoms or ions. Coefficients of absorption in lines always are very gerat — considerably larger than in continuous spectrum. Therefore, effective temperature in lines practically exactly coincides with temperature at the actual surface of the body (lines are "cut" in spectrum of radiation of body).

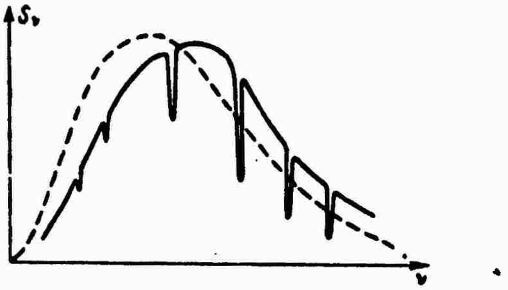

Fig. 2.8. Schematic representation of spectrum of radiation of body with temperature decreasing toward its surface. Low frequencies are absorbed more strongly than high ones. Dotted line shows Planck spectrum corresponding to average effective temperature of radiation. In the spectrum there are cut lines of selective absorption. Flux at centers of these lines is practically equal to Planck flux corresponding to temperature of surface of body.

For comparison, in Fig. 2.8 the dotted line shows Planck spectrum corresponding to integral effective temperature, which is average with respect to spectral temperatures. In virtue of the definition of integral effective temperature, areas bounded by solid and dotted curves are exactly equal.

In Chapter V we will see that coefficients of continuous absorption at high temperatures are not smooth functions of frequency, but experience jumps. Accordingly there appear jumps also in spectrum of radiation of body. (This is not shown in Fig. 2.8, which pertains to smooth dependence of $\varkappa_\nu'$ on ν).

Frequently, during optical measurements of incondescence of heated bodies, there is used idea of color temperature. Color temperature is defined as the temperature of an ideal black body which would give ratio of brightnesses in two different spectral sections (for instance, in red and blue regions of spectrum) equal to that measured by experiment. Using definitions of effective and color temperatures, it is easy to write relationship between them. Let us assume that luminance temperatures at frequencies ν_1 and ν_2 are T_1 and T_2, and color temperature is T_{12}. Considering for simplicity that both lines, ν_1 and ν_2, lie in Wien region of spectrum, i.e., $h\nu_1/kT_1 >> 1$, $h\nu_2/kT_2 >> 1$, we will obtain

$$S_{\nu_1} \sim \nu_1^3 e^{-\frac{h\nu_1}{kT_1}}, \quad S_{\nu_2} \sim \nu_2^3 e^{-\frac{h\nu_2}{kT_2}};$$

$$\frac{S_{\nu_1}}{S_{\nu_2}} = \frac{\nu_1^3}{\nu_2^3} e^{-\left(\frac{h\nu_1}{kT_1} - \frac{h\nu_2}{kT_2}\right)} = \frac{\nu_1^3}{\nu_2^3} e^{-\left(\frac{h\nu_1 - h\nu_2}{kT_{12}}\right)},$$

whence

$$\frac{\nu_1 - \nu_2}{T_{12}} = \frac{\nu_1}{T_1} - \frac{\nu_2}{T_2}. \qquad (2.54)$$

If temperature of body is more or less constant in radiating layers for the whole main spectrum near the surface, color temperature is frequently nearer to true temperature of body than luminance temperatures; this circumstance is used in pyrometry, during optical measurements of temperature of bodies.

Let us note that in case of a nonuniformly heated "gray" body, for which coefficient of absorption $\varkappa_\nu'$ does not depend on frequency, $\varkappa_\nu' \equiv \varkappa'$, effective temperature of different frequencies all the same depends on frequency. Only for very small quanta, lying in Rayleigh-Jeans region of the spectrum $h\nu/kT \ll 1$, does frequency drop out of formula (2.52). In this case effective temperatures for all these frequencies turn out to be identical.

§ 9. Motion of Substance Taking into Account Radiant Heat Exchange

Above it was shown how there can be found field of radiation in body or radiation going out from surface of body, if state of substance, i.e., distribution of temperature and density in the medium, are known. Let us consider how there is formulated problem of joint determination of state and motion of substance and field of radiation in the case when transfer of radiation and interaction of radiation with substance render an essential influence on state and motion of the medium (gas). Thus motion of substance will always be assumed to be non-relativistic, i.e., it will be considered that speed is much less than velocity of light.

If temperature is not too high, and density of gas is not too low, energy density and radiation pressure are negligible as compared to energy and pressure of substance. Let us compare for estimate density of equilibrium radiation $U_p = \frac{4\sigma T^4}{c}$ with thermal energy of unit of volume of monatomic gas $E = \frac{3}{2}nkT$ (n is number of particles in 1 cm^3). For instance, at $n = 2.67 \cdot 10^{19}$ 1 cm^3, which corresponds to number of molecules in air of normal density, both energies coincide at a temperature of 900 000°K. In reality, energy of radiation becomes comparable with energy of substance at still higher temperatures, since during heating, atoms are ionized, which first, leads to increase of number of particles in 1 cm^3 and, secondly, adds to the thermal energy the energy expended in ionization.* Thus, in real air of normal density, energy of radiation is comparable with internal energy of substance only at a temperature of about 2 700 000°K. In strongly rarefied gas, energy of equilibrium radiation becomes comparable with energy of substance at lower temperatures (roughly speaking, temperature at which both energies are equal is proportional to $n^{1/3}$). However, in this case, during comparison of energies it is necessary to use caution, since in very rarefied gas mean free path of radiation is great, and if dimensions of gas mass are not great enough, density of radiation may be much less than equilibrium density (see below).

Pressures of radiation and substance are approximately in the same ratio as energies. Indeed, radiation pressure (during isotropy

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*About thermodynamic functions of gases at high temperatures, see Chapter III.

of field of radiation) $p_\nu = U/3$, and pressure of substance $p = (\gamma - 1)E$, where at high temperatures adiabatic index γ usually has value in interval from 5/3 to ~1.15 depending upon element composition of gas, temperature, and density.

Thus, at not too high temperatures and not too low densities of substance, energy density and radiation pressure practically do not affect energy balance and gas-dynamic motion of substance. The influence of radiation on energy balance and motion of gas is different: losses of energy by a heated body due to radiation and, in general, radiant heat exchange in the medium can become considerable. These effects frequently play a role at much lower temperatures, when energy and pressure of radiation are known to be very small.

Cause of these phenomenon consists of sharp difference in velocities of substance u under usual conditions and velocity of light c; $u \ll c$. Due to difference in velocities, energy flows of substance and radiation can be comparable with each other, even if energy density of radiation is much less than energy density of substance. For instance, in the extreme case, when all quanta move in one direction, energy flow of radiation is equal to $S = Uc$; flux of energy of substance is on the order of Eu, i.e., Uc can be on the order of or greater than Eu even at $U \ll E$ due to the fact that $c \gg u$. Energy flows of radiation and substance frequently are comparable even in the more real case, when field of radiation is relatively isotropic, and the resultant radiation flux S, which is equal to difference between unidirectional fluxes, is considerably less than its limiting value Uc, which corresponds to sharply expressed anisotropy of field of radiation.

As will now be shown, magnitude of losses of energy or, conversely, energy release in substance due to interaction with radiation, are determined by divergence of radiation flux, so that comparison of energy flows of radiation and substance can characterize the role of radiant heat exchange in a medium.

We will find quantity of energy q lost by a unit of volume of matter in 1 sec by radiation. It is the difference between energy emitted by substance and energy of radiation absorbed by substance.

Difference between emission and absorption of radiation of frequency ν (per unit interval of frequencies) and direction Ω (per unit of solid angle) in 1 sec in 1 cm^3 stands in right side of equation of transfer of radiation (2.28). In order to obtain total resultant loss of energy by substance in 1 cm^3 in 1 sec q, it is necessary to integrate this quantity over all solid angle and over all spectrum, i.e.,

$$q = \int_0^\infty d\nu \int d\Omega \varkappa'_\nu (I_{\nu p} - I_\nu) = c \int_0^\infty d\nu \varkappa'_\nu (U_{\nu p} - U). \tag{2.55}$$

First term in parentheses corresponds to spontaneous emission, and second — to absorption after subtracting "re-emission."

With help of equation of continuity for radiation (2.29), in which according to the earlier made remark about quasi-steady-state character of transfer of radiation it is possible to omit time derivative, we will find that resultant loss of energy is equal to divergence of integrated flux of radiation:

$$q = \int_0^\infty \operatorname{div} S_\nu \, d\nu = \operatorname{div} S. \tag{2.56}$$

If substance emits more than it absorbs, it loses energy by radiation (is cooled by radiation), and $q > 0$; if there is absorbed more energy than there is emitted, substance is heated by radiation and "loss of energy" is negative, q < 0 (i.e., energy release, which is equal to -q, is positive).

We will form equations of gas dynamics taking into account radiant heat exchange, but disregarding energy and pressure of radiation.

First equation — equation of continuity — remains unchanged. Also equation of motion does not change, inasmuch as radiation pressure will be disregarded. Only in equation of energy should there be introduced a term of losses of energy by radiation (energy density of radiation and work of forces of radiation pressure will be disregarded). Equation of energy (1.10) will be written in the form*

$$\frac{\partial}{\partial t}\left(\rho\varepsilon+\frac{\rho u^2}{2}\right)=-\operatorname{div}\left[\rho u\left(\varepsilon+\frac{p}{\rho}+\frac{u^2}{2}\right)\right]-q, \tag{2.57}$$

or, replacing q by divergence of flux S,

$$\frac{\partial}{\partial t}\left(\rho\varepsilon+\frac{\rho u^2}{2}\right)=-\operatorname{div}\left[\rho u\left(\varepsilon+\frac{p}{\rho}+\frac{u^2}{2}\right)+S\right]. \tag{2.58}$$

Thus, to total hydrodynamic energy flow there is added energy flow of radiation. If we transform gas-dynamic equation of energy to entropy form (see § 1 Chapter I), we will obtain

$$\rho T\frac{d\Sigma}{dt}=-q=-\operatorname{div} S, \tag{2.59}$$

where Σ is specific entropy of substance.

Finding of field of radiation and distribution of temperature in medium under conditions when radiant heat exchange considerably affects energy balance of substance is connected with large mathematical difficulties. Differential equation of transfer with respect to coordinates (2.34), which describes field of radiation, is formulated for spectral intensity of radiation propagated in definite direction. In equation of energy balance (2.57) there are contained quantities q ~~or S,~~ which are integrated over spectrum, as well as over directions.

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*It is assumed that, besides radiant heat exchange, no sources of energy, and also no other irreversible processes exist.

Thus, system of equations of transfer and energy has integrodifferential character; it contains double integration: over spectrum and over angles.

Mathematical simplifications of integrodifferential system proceed by way of approximate description of spectral and angular distributions, in order to avoid its "integral character." Influence of spectral distribution on energy balance appears in connection with dependence of coefficient of absorption on frequency. Exclusion of spectral characteristics from consideration is possible only if coefficient of absorption $\varkappa_\nu'$ does not depend on frequency: $\varkappa_\nu' \equiv \varkappa'$. In this case of "gray substance," equation of transfer (2.34) after integration over frequencies is written directly for intensity integrated over the spectrum $I = \int_0^\infty I_\nu d\nu$:

$$\Omega\nabla I = \varkappa'(I_p - I), \qquad (2.60)$$

and in formula (2.55), for losses of energy by substance, it is also possible to produce integration over spectrum:

$$q = \varkappa' \int (I_p - I)\, d\Omega = c\varkappa'(U_p - U). \qquad (2.61)$$

In general, coefficients of absorption in gasses at high temperatures very strongly depend on frequency, and the idea of "gray material" constitutes a considerable idealization. It is very useful in the sense that it permits clarification of behavior of phenomena which are not connected with spectral distribution of radiation. However, in certain important limiting cases, which we will discuss below, introduction in the appropriate way of coefficient of absorption $\varkappa'$, averaged over frequencies, which allows us to exclude from consideration spectral characteristics of radiation and to go over to formulas (2.60), (2.61), corresponds to the essence of the matter.

To the question about approximate description of angular distribution of field of radiation will be dedicated the following two paragraphs.

§ 10. Diffusion Approximation

Losses of energy of substance by radiation q, as can be seen from formulas (2.55), (2.56), in explicit form do not depend on angular distribution of radiation and are determined only by quantities integrated over directions: radiation density or flux. If it were possible to form instead of equation of transfer for intensity of radiation (which depends on direction) some other equations, which would directly be obeyed by quantities integrated over directions, density, and radiation flux, then question about angular distribution of radiation in examining of influence of radiation on state and motion of substance in general would not appear. One such equation already exists: this is the exact equation of continuity (2.29), which in quasi-steady-state case states that:

$$\operatorname{div} \mathbf{S}_\nu = c\varkappa_\nu' (U_{\nu p} - U_\nu). \tag{2.62}$$

The second relationship, which relates flux and density of radiation and closes the system of equations, can be obtained only approximately. Equation (2.62) was found by means of integration of equation of transfer over angles. Let us multiply now equation of transfer (2.34) by unit direction vector $\mathbf{\Omega}$ and again integrate over angles. Noticing that integral of term $\varkappa_\nu' I_{\nu p}$, which does not depend on direction, becomes zero, and taking into account definition of flux (2.3), we will obtain

$$\int \mathbf{\Omega} \cdot \mathbf{\Omega} \nabla I_\nu \cdot d\mathbf{\Omega} = -\varkappa_\nu' \mathbf{S}_\nu. \tag{2.63}$$

In isotropic field of radiation flux $S_\nu = \int \Omega I_\nu \, d\Omega$ becomes zero. Integral in left side of equality for intensity I_ν not depending on angle is easy to calculate*

$$\int \Omega \cdot \Omega I_\nu \cdot d\Omega = \frac{1}{3}\int \nabla I_\nu \, d\Omega = \frac{c}{3}\nabla U_\nu. \tag{2.64}$$

Equality to zero of this expression indicates that isotropy of field of radiation is connected with constancy of density in space. If field of radiation is anisotropical, flux and integral (2.63) are different from zero. However, in case of weak anisotropy, in first approximation integral can be, as before, represented in form (2.64), if we consider intensity weakly depending on angles to be constant. This gives approximate relation of flux to radiation density

$$S_\nu = -\frac{l'_\nu c}{3}\nabla U_\nu, \tag{2.65}$$

where $l'_\nu = 1/\varkappa'_\nu$ is mean free path for absorption of radiation (corrected for stimulated emission).

If we divide both sides of equality (2.65) by energy of quantum $h\nu$, we will obtain relation between flux of quanta of given frequency J_ν and their density N_ν, which is usual for process of diffusion of particles,

$$J_\nu = -D_\nu \nabla N_\nu, \quad D_\nu = \frac{l'_\nu c}{3}.$$

Coefficient of "diffusion" of quanta D_ν is analogous to coefficient of diffusion of atoms or molecules; c is velocity of "motion" of quanta, l'_ν is their mean free path.

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*We will find i-th component of vector integral, replacing vector operator $\Omega\nabla$ by coordinate expression $\Omega_k \, \partial/\partial x_k$ and considering summation over the twice met indices:

$$\int \Omega_i \Omega_k \frac{\partial I_\nu}{\partial x_k} d\Omega = \frac{\partial I_\nu}{\partial x_k}\int \Omega_i \Omega_k \, d\Omega = \frac{\partial I_\nu}{\partial x_k}\cdot\frac{4\pi}{3}\delta_{ik} = \frac{4\pi}{3}\frac{\partial I_\nu}{\partial x_i} = \frac{c}{3}\frac{\partial U_\nu}{\partial x_i},$$

since $\int I_\nu \, d\Omega = 4\pi I_\nu = cU_\nu$; hence there follows (2.64).

However, between diffusion of atoms and "diffusion" of quanta there is an essential distinction. An atom during collision does not disappear, but only changes direction of its motion (in an arbitrary way for the case of isotropic scattering); mean free path included in coefficient of diffusion is mean free path with respect to collisions. A quantum passing on the average over distance l_ν', is absorbed by substance, and under conditions of thermodynamic equilibrium of substance its energy due to collisions with atoms, electrons, etc., is distributed in substance in accordance with laws of statistical equilibrium. At the place of absorption there are emitted new quanta of different frequencies and in arbitrary directions. Considering process of "diffusion" of quanta of given frequency, we distinguish among the newly generated quanta only quanta of the same frequency. The process proceeds as if the quantum flew, was absorbed, and then again was "generated," and after "generation" can fly with equal probability in any direction, which corresponds to process of isotropic scattering of atoms during collision.*

Just as during diffusion of atoms, condition of applicability of diffusion approximation is smallness of density gradient of radiation. The latter should change little at a distance on the order of mean free path of radiation l_ν'. For small gradients field of radiation is almost isotropic, and this condition was assumed at basis of derivation of diffusion equation (2.65). Really, to a given point quanta arrive

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*If we consider transfer of radiation, taking into account scattering of quanta, then during weak anisotropy, as before, there is obtained diffusion relationship of type (2.65), in which there stands mean free path corresponding to total attenuation factor, which is equal to sum of coefficients of absorption and scattering. If scattering is anisotropic, then, just as during diffusion of atoms, instead of scattering coefficient there appears transport coefficient $\varkappa_S(1 - \overline{\cos\theta})$, where $\overline{\cos\theta}$ is average cosine of scattering angle.

mainly from region with dimensions on the order of mean free path. If radiation density in this region is almost constant, then quanta arrive at given point from all directions equally, which leads to isotropy of field of radiation in it.

Near boundary between the medium and vacuum, density changes strongly at distance on the order of mean free path, and anisotropy of angular distribution of quanta is great — quanta chiefly fly from body in the direction of the vacuum, since they do not proceed from the vacuum. Therefore, near boundary with vacuum, diffusion approximation can lead to noticeable errors.

Gradients of density are small and diffusion approximation is accurate in case of optically thick bodies. If x is characteristic scale, on which density of radiation noticeably changes (x is on the order of dimensions of body), then diffusion flux in order of magnitude is equal to

$$S_\nu = -\frac{l'_\nu c}{3}\nabla U_\nu \sim \frac{l'_\nu}{x} c U_\nu .$$

The greater the optical thickness of the body x/l'_ν is, the less density of radiation changes on mean free path (this change is on the order of $l'_\nu \nabla U_\nu \sim \frac{l'_\nu}{x} U_\nu$), the smaller flux S_ν, is as compared to quantity $U_\nu c$, and the more accurate the diffusion approximation is.

If optical thickness of body is on the order of unity, $l'_\nu/x \sim 1$ and $S_\nu \sim cU_\nu$. In case of an optically thin body $l'_\nu/x > 1$, and flux estimated by diffusion formula would have to become larger than cU_ν. In reality this is impossible and simply indicates the inapplicability of diffusion formula for optically thin bodies.

Flux S_ν never can be larger than cU_ν. Equality $S_\nu = cU_\nu$ corresponds to the case when all quanta fly strictly in one direction, i.e., it corresponds to the most sharply expressed anisotropy. Quantity

cU_ν sometimes is called kinetic flux. Ratio of flux to kinetic S_ν/cU_ν, which in the diffusion approximation is on the order of inverse optical thickness of body l_ν'/x, is a measure of anisotropy of field of radiation: during complete isotropy $S_\nu/cU_\nu = 0$; if all quanta fly in one direction $S_\nu/cU_\nu = 1$. Ratio S_ν/cU_ν always is contained within limits $0 < \frac{S_\nu}{cU_\nu} < 1$. Dependence of flux on degree of anisotropy of angular distribution of radiation at a given density of it is schematically illustrated by polar diagram for intensity (Fig. 2.9).

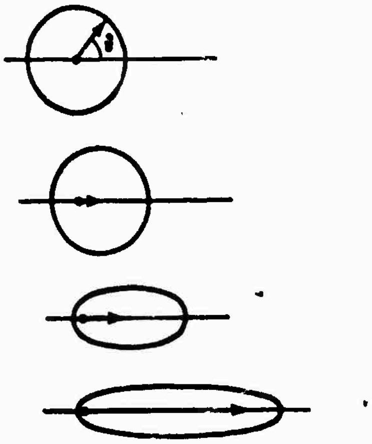

Fig. 2.9. Polar diagrams for distribution of intensity of radiation over angle for various degrees of anisotropy. Magnitude of intensity at given angle ϑ is characterized by length of radius-vector drawn from center. Length of arrow characterizes value of flux. Equality of radiation densities in all cases is schematically described by equality of areas of all figures.

Areas of all figures are identical and correspond to density of radiation, and lengths of arrows correspond to fluxes. Fields of radiation of various densities can also lead to the same flux. The greater the density for a given flux, the smaller is S_ν/cU_ν, and the more isotropic should be the field of radiation.

Equations of diffusion approximation (2.62), (2.65) constitute a system of two differential equations in two unknown functions of coordinates: density and flux of radiation. To them it is necessary to assign boundary conditions on boundaries between media with different optical properties (with different "coefficients of diffusion"). From the condition of continuity of intensity of radiation there follows continuity of density and flux on boundaries. A discontinuity in density in diffusion approximation (2.65) would imply an infinity of flux, and a discontinuity in flux would indicate radiation build-up, i.e., a non-steady-state character (see equation (2.29)).

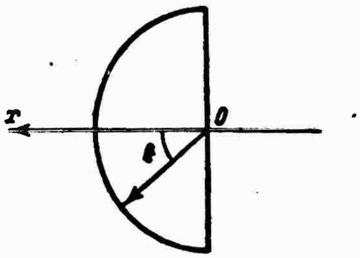

Fig. 2.10. Polar diagram for distribution of intensity on boundary x = 0 of body with vacuum. Vacuum on the right, medium on the left.

Special consideration is required by case of boundary between medium and vacuum. Inasmuch as quanta do not proceed from vacuum, field of radiation on boundary with vacuum is strongly anisotropic (all quanta fly only in the direction toward the vacuum), and, strictly speaking, diffusion approximation here is inapplicable. Approximate condition on boundary can be written proceeding from the following consideration. Let us assume (and this for optically thick bodies is not very far from the truth) that radiation going out from surface of body in a hemisphere directed toward the vacuum is distributed over angles isotropically; in the other hemisphere, intensity is equal to zero: quanta do not arrive from the vacuum (corresponding polar diagram is shown in Fig. 2.10). We obtain then that on boundary with vacuum

$$S_\nu = \frac{cU_\nu}{2}, \qquad (2.66)$$

where flux is directed along outward normal to surface. Factor 1/2 appears as average cosine of angle of directions of motion of quanta for their isotropic distribution in the hemisphere.*

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*Really, $S_\nu = \int_{\text{hemisphere}} \Omega I_\nu \, d\Omega$; $S_\nu = \int_0^{\pi/2} \cos\vartheta I_\nu(\vartheta) \, 2\pi \sin\vartheta \, d\vartheta = 2\pi I_\nu \cdot \frac{1}{2} = \pi I_\nu$, but $cU_\nu = \int_{\text{hemisphere}} I_\nu \, d\Omega = \int_0^{\pi/2} 2\pi \sin\vartheta \, d\vartheta I_\nu = 2\pi I_\nu$, whence there follows formula (2.66).

Formula (2.66) formally ensues from relationships of the diffusion approximation. It is easy to verify that the following expression for intensity leads to diffusion equations (2.62), (2.65):

§ 11. "Forward-Backward" Approximation

We will consider one more method of approximate consideration of angular distribution of radiation, which is sometimes applied in two-dimensional problems of radiation transfer. This method is known as the Schwartzschild approximation or "forward-backward" approximation. Let us combine all quanta moving in the positive direction of x-axis at angles ϑ from 0 to $\pi/2$ ("forward") into one group, and those moving in opposite direction ("backward") at angles ϑ from $\frac{\pi}{2}$ to π in another group (Fig. 2.11). We will approximately consider angular distributions in each of the two hemispheres as isotropic and designate intensities in directions "forward" and "backward" by I_1 and I_2 (index of frequency ν for brevity will be omitted). Density and flux of

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[FOOTNOTE CONT'D FROM PRECEDING PAGE].

$$I_\nu(\Omega) = \frac{cU_\nu}{4\pi}\left[1+\frac{3\Omega S_\nu}{cU_\nu}\right] = \frac{cU_\nu}{4\pi}\left[1+3\cos\vartheta\,\frac{S_\nu}{cU_\nu}\right],$$

where ϑ is angle between direction Ω and direction of flux S_ν. Taking x-axis in direction of flux, we will calculate unidirectional fluxes in positive and negative directions of x-axis. We will obtain

$$S_{\nu+} = \frac{cU_\nu}{4} + \frac{S_\nu}{2}, \quad S_{\nu-} = -\frac{cU_\nu}{4} + \frac{S_\nu}{2} \qquad (2.67)$$

(it is clear that $S_\nu = S_{\nu+} + S_{\nu-}$, as it must be). Applying these formulas to boundary between body and vacuum (x-axis is directed toward the vacuum) and assuming that unidirectional flux from vacuum $S_{\nu-} = 0$, we will obtain $S_\nu = S_{\nu+} = \frac{cU_\nu}{2}$, i.e., formula (2.66). Formulas (2.67) have greater force than the expression for intensity. This can easily be verified if we extend formula for intensity to a point at the boundary.

In direction of negative x-axis, for instance, $\cos\pi = -1$ and $I_\nu = -\frac{cU_\nu}{8\pi} < 0$, which is physically senseless. The whole fact is that diffusion formula for intensity is suitable only for weak anisotropy, when second term in parentheses is much less than unity.

radiation thus are equal to

$$U=\frac{1}{c}\int I\,d\Omega=\frac{2\pi}{c}\int_0^{\pi/2} I_1\sin\vartheta\,d\vartheta+\frac{2\pi}{c}\int_{\pi/2}^{\pi} I_2\sin\vartheta\,d\vartheta=\frac{2\pi}{c}(I_1+I_2), \tag{2.68}$$

$$S=\int\cos\vartheta I\,d\Omega=2\pi\int_0^{\pi/2} I_1\cos\vartheta\sin\vartheta\,d\vartheta+2\pi\int_{\pi/2}^{\pi} I_2\cos\vartheta\sin\vartheta\,d\vartheta=\pi(I_1-I_2). \tag{2.69}$$

Hence, incidentally, there is graphically represented the degree of anisotropy:

$$\frac{S}{cU}=\frac{I_1-I_2}{2(I_1+I_2)}\to 0 \text{ for } I_1\approx I_2.$$

On boundary between medium and vacuum, if x-axis is directed along outward normal to surface, we have $I_2 = 0$ and $\frac{S}{cU} = \frac{1}{2}$, i.e., condition (2.66).

In order to form equation for average "unidirectional" intensities I_1 and I_2, we will average transfer equation for plane case:

$$\cos\vartheta\frac{dI}{dx}=\varkappa'(I_p-I) \tag{2.70}$$

over one and over the other hemisphere. We will obtain thus (average cosine $\overline{\cos\vartheta} = \pm\frac{1}{2}$):

$$\frac{1}{2}\frac{dI_1}{dx}=\varkappa'(I_p-I_1); \quad -\frac{1}{2}\frac{dI_2}{dx}=\varkappa'(I_p-I_2). \tag{2.71}$$

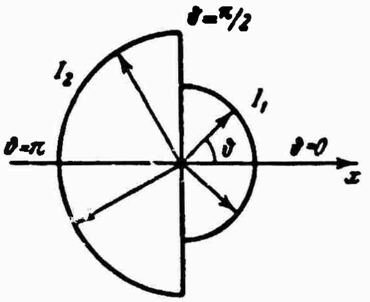

Fig. 2.11. Polar diagram for distribution of intensity of radiation in "forward-backward" approximation. In this case flux is directed to the left.

This pair of equations serves for determination of average intensities in both hemispheres. By adding and substracting them, it is easy to go over to equations for density and flux ($I_p = cU_p/4\pi$):

$$\frac{dS}{dx}=\varkappa'(U_p-U); \quad S=-\frac{l'c}{4}\frac{dU}{dx}. \tag{2.72}$$

The first of the equations is exact continuity equation (2.62), and the second one coincides with approximate equation of diffusion approximation (2.65), with only the difference that here "coefficient of diffusion" is equal to $l'c/4$ instead of $l'c/3$.

By considering equations (2.71) as linear differential equations in functions I_1 and I_2, it is possible to write their solution in integral form:

$$I_1=\int_{\tau}^{\infty} I_p \exp\left[-2(\tau'-\tau)\right] 2\,d\tau'; \quad I_2=\int_{0}^{\tau} I_p \exp\left[-2(\tau-\tau')\right] 2\,d\tau'.$$

Here coordinate x is replaced by optical thickness by the formulas:

$$d\tau=\varkappa'\,dx, \quad \tau=\int_0^x \varkappa'\,dx.$$

By adding and subtracting expressions for I_1 and I_2 and substituting $I_p = cU_p/4\pi$, we will obtain approximate integral formulas for density and flux in the "forward-backward" approximation.

$$\left.\begin{aligned} U&=\frac{1}{2}\int_{\tau}^{\infty} U_p e^{-2(\tau'-\tau)}2\,d\tau+\frac{1}{2}\int_{0}^{\tau} U_p e^{-2(\tau-\tau')}2\,d\tau,\\ S&=\frac{c}{4}\int_{\tau}^{\infty} \cdot\, p^{-\ (\tau'-\tau)}2\,d\tau-\frac{c}{4}\int_{0}^{\tau} U_p e^{-2(\tau-\tau')}2\,d\tau. \end{aligned}\right\} \qquad (2.73)$$

In general, the diffusion approximation in case of weak anisotropy is better founded than the "forward-backward" approximations, which little differs from it. However, density and flux in diffusion approximation are impossible to represent in integral form without contradicting differential equations, as can be done in "forward-backward" approximation. Therefore, sometimes, when integral form of equations is more convenient, it is more advantageous to use the latter approximation.

§ 12. Local Equilibrium and Approximation of Radiant Thermal Conduction

In an infinite medium with constant temperature in steady state, radiation is thermodynamically equilibrium. Intensity of it does not depend on direction, and is determined by formula of Planck. To a certain point of space there arrive quanta generated in neighborhood of this point at distances of not more than several mean free paths; quanta generated far off do not reach the point; they are absorbed along their path. Consequently, in creation of equilibrium intensity at a given point, there participates only its immediate environment. Even if temperature far off is different from temperature of this neighborhood, this in practice does not affect intensity of radiation at the considered point. This means that if in a sufficiently extended, optically thick medium temperature is not constant, but changes sufficiently slowly with distance, so that its changes are small at distances on the order of mean free path of radiation, intensity at some point of space will be very close to equilibrium on temperature which corresponds to temperature of the given point. Thus intensity will be nearer to equilibrium, the less temperature changes at distances on the order of mean free path. In particular, radiation will be nearer to equilibrium at those frequencies which are absorbed more strongly, and for which mean free path l'_{ν} is less. If temperature gradient is so small that changes of temperature are small at distances on the order of the largest of mean free paths l'_{ν} for all frequencies playing an important role in equilibrium radiation of given temperature, then radiation will be equilibrium in practically the whole spectral interval which is characteristic for temperature of the given point. Intensity of radiation depending upon frequency will thus be described by Planck function with temperature of this point.

Such a state, when radiation at every point of medium with variable temperature is very close to equilibrium, radiation, which corresponds to temperature of the point, is spoken of as local thermodynamic equilibrium of radiation with substance.

Condition of existence of local equilibrium — smallness of gradients in an extended, optically thick medium — serves at the same time as justification of the diffusion approximation in examining of radiation transfer. In the diffusion approximation, radiation flux is proportional to gradient of radiation density. But if density of radiation is close to equilibrium, then it is possible approximately to replace true density in formula for flux by equilibrium density at given point. Thus, under conditions of local equilibrium, spectral flux is approximately equal to

$$S_\nu = -\frac{l'_\nu c}{3} \nabla U_{\nu p}. \tag{2.74}$$

Total flux is

$$S = \int_0^\infty S_\nu \, d\nu = -\frac{c}{3} \int_0^\infty l_\nu \nabla U_{\nu p} \, d\nu. \tag{2.75}$$

We will take from under the integral sign a certain mean value of mean free path, which we will designate by l. If we consider that $\int_0^\infty U_{\nu p} \, d\nu = U_p = 4\sigma T^4/c$, then formula (2.75) gives

$$S = -\frac{lc}{3} \nabla U_p = -\frac{16\sigma l T^3}{3} \nabla T. \tag{2.76}$$

Energy flow of radiation under conditions of local equilibrium is proportional to temperature gradient; i.e., radiation transfer has the character of thermal conduction or, so to speak, radiant thermal conduction, where coefficient of thermal conductivity is equal to $\frac{16\sigma IT^3}{3}$ and depends on temperature.

Loss of energy of substance by radiation q according to formula (2.56) is equal to divergence of flux of radiant thermal conduction, exactly as in the case of usual molecular thermal conduction, and is determined only by temperature of substance at given point, average mean free path, which for given substance is function of temperature and density, and by their derivatives with respect to coordinates.

Comparison of formulas (2.75) and (2.76) gives law of averaging of mean free path over spectrum which leads to correct value of flux of radiant energy under conditions when radiant heat exchange has character of thermal conduction. Noticing that $U_{\nu p}$ and U_p depend on coordinates only through dependence on temperature, we will obtain

$$l=\frac{\int\limits_0^\infty l'_\nu \frac{dU_{\nu p}}{dT}\,d\nu}{\frac{dU_p}{dT}}=\frac{\int\limits_0^\infty l'_\nu \frac{dU_{\nu p}}{dT}\,d\nu}{\int\limits_0^\infty \frac{dU_{\nu p}}{dT}\,d\nu}. \tag{2.77}$$

By differentiating equilibrium density of radiation taken by the Planck formula with respect to temperature and going over in the integral to dimensionless variable of integration $u = \frac{h\nu}{kT}$, we will find law of averaging of mean free path:

$$l=\int\limits_0^\infty l'_\nu G(u)\,du, \tag{2.78}$$

where weighting factor G(u) is equal to

$$G(u)=\frac{15}{4\pi^4}\frac{u^4 e^{-u}}{(1-e^{-u})^2}. \tag{2.79}$$

Quantity l, obtained by means of averaging of mean free path l'_ν with weighting factor G(u), called Rosseland average mean free path or simply Rosseland mean free path. If we express mean free path l'_ν, corrected for stimulated emission, in terms of coefficient of true absorption $l'_\nu = 1/\varkappa'_\nu = 1/\varkappa\,(1 - e^{-u})$, then formulas (2.78), (2.79) can be rewritten in the form

$$l=\int\limits_0^\infty \frac{1}{\varkappa_\nu} G'(u)\,du, \quad G'(u)=\frac{15}{4\pi^4}\frac{u^4 e^{-u}}{(1-e^{-u})^3}. \tag{2.80}$$

Rosseland weighting factor has maximum at $h\nu \approx 4kT$, i.e., main role in transfer of energy is played by large quanta with energy a few times higher than kT.

According to the formula (2.76), radiation flux is greater, the larger the coefficient of thermal conductivity, i.e., the longer the mean free path. One should not forget that this dependence is accurate only as long as mean free path is not too great, in order that there is not violated the condition of local equilibrium and formula (2.76) has meaning. As we will see later in the opposite limiting case, when mean free path of radiation is larger than characteristic dimensions of the body, radiation flux, conversely, decreases with increase of mean free path.

§ 13. Interrelation of Diffusion Approximation and Approximation of Radiant Thermal Conduction

Usually in astrophysics it is accepted to identify ideas of diffusion approximation and radiant thermal conduction with each other. This is connected with the fact that in optically thick bodies with small gradients, such as stars and stellar photospheres, there always are simultaneously satisfied conditions leading to weak anisotropy of field of radiation, i.e., to diffusion coupling of flux with gradient of radiation density, and to existence of local equilibrium, i.e., possibility of replacement of U_ν by $U_{\nu p}$. Estimate shows that, in general, for small gradients in optically thick bodies, deviation from local equilibrium is even less than degree of anisotropy, i.e., if diffusion approximation is accurate, then local equilibrium all the more so exists. Really, let us assume that body has dimensions on the order of x, which are the characteristic scale for gradients of temperature, density and radiation flux. From equations of diffusion approximation (2.62), (2.65), it follows that in order of magnitude

$$\frac{S_\nu}{x} \sim \frac{c(U_{\nu p}-U_\nu)}{l'_\nu}, \quad S_\nu \sim \frac{l'_\nu}{x} cU_\nu,$$

whence

$$\frac{U_{\nu p}-U_\nu}{U_\nu} \sim \left(\frac{l'_\nu}{x}\right)^2.$$

If degree of anisotropy, which is characterized ratio of diffusion flux to kinetic flux, $S_\nu/cU_\nu \approx l'_\nu/x$, is small and $l'_\nu/x \ll 1$, then relative deviation of density of radiation from equilibrium is a quantity of the second order of smallness.

However, considering problems with more complicated conditions than in stellar photospheres, it is convenient nevertheless to draw a clear line between diffusion approximation and radiant thermal conduction approximation, meaning by the diffusion approximation only a method of approximate description of angular distribution of radiation in which radiation flux is assumed to be proportional to gradient of true density, even if it very strongly differs from equilibrium. This can be considered as a method allowing us to clarify properties of phenomena of transfer of strongly non-equilibrium radiation which are not connected with character of angular distribution of quanta, since strict calculation of the latter is connected with large mathematical difficulties. Diffusion approximation, which leads in certain cases to considerable errors, as a rule, nevertheless, does not distort qualitative picture of phenomena of radiation transfer, even when distribution over angles is strongly anisotropic. This permits us to use it for approximate solution of different problems in which radiation is essentially non-equilibrium, and use of approximation of radiant thermal conduction, which subjects temperature of substance to corresponding equations, frequently contradicts physical meaning.

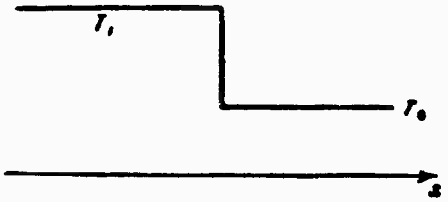

Fig. 2.12. Schematic profile of temperature in shock wave.

Let us give an example. Let us assume, that we are interested in field of radiation in body with a sharp jump of temperature on the surface dividing highly heated and cold regions, as is shown in Fig. 2.12 (case which is typical for a shock wave). In region with high temperature, density of radiation U_1 is great and on the order of equilibrium $U_{p1} = 4\sigma T_1^4/c$. In region of low temperature quanta practically are not emitted, and density of radiation in it is determined by flux going out from surface of heated region, i.e., density of radiation also is proportional to U_1 and much higher than equilibrium $U_{p0} = 4\sigma T_0^4/c$, since $T_1 \gg T_0$. This case, as we see, is extraordinarily far from local equilibrium and radiant thermal conduction. Meanwhile, diffusion approximation for description of angular distribution leads to qualitatively correct result, which is that if cold medium absorbs light, then density and radiation flux drop according to distance from heated surface into the cold medium, where scale of distance for noticeable attenuation of these quantities is mean free path for absorption of quanta in cold medium. Thus, in this case diffusion equations in cold medium not emitting quanta take the form

$$\frac{dS_\nu}{dx} = -\frac{cU_\nu}{l_\nu}, \quad S_\nu = -\frac{l_\nu c}{3}\frac{dU_\nu}{dx}$$

or, in terms of optical thickness measured from temperature jump $\tau_\nu = \int_0^x \varkappa'_\nu \, dx$,

$$\frac{dS_\nu}{d\tau_\nu} = -cU_\nu, \quad S_\nu = -\frac{c}{3}\frac{dU_\nu}{d\tau_\nu}.$$

These equations give solutions for density and flux:

$$S_\nu = \frac{cU_\nu}{\sqrt{3}} \sim e^{-\sqrt{3}\tau_\nu},$$

which qualitatively correctly reflects drop of these quantities.

Exact consideration of angular distribution, which is possible in the given simple case, leads to a somewhat different law of decrease of flux and density of radiation in cold region containing not usual, but exponential integrals (see work [5]):

$$S_\nu \sim E_3(\tau_\nu), \quad U_\nu \sim E_2(\tau_\nu).$$

At optical distances from temperature jump on the order of one or several units, exact formulas give values of the same order as diffusion formulas. If we in the considered problem used approximation of radiant thermal conduction, then we would have, in particular, the temperature jump of the substance being spread out since with temperature jump flux S ~ dT/dx turns out to be infinite.

In general, diffusion approximation always gives qualitatively reasonable results. For instance, in such an extremely "non-diffusion" case as when there is extremely pronounced anisotropy of angular distribution of quanta, and all quanta move in cold medium in one direction, flux is equal to $S_\nu = cU_\nu$. From exact continuity equation (2.62) it is obtained thus that flux, as during diffusion, is proportional to gradient of density $S_\nu = -l'_\nu c \frac{dU_\nu}{dx}$ (x-axis is directed along light beam) with proportionality factor three times as large as usual coefficient of diffusion. This case of pure absorption of parallel beam of light in a non-radiating medium has an exact solution:

$$S_\nu = cU_\nu \sim e^{-\tau_\nu}, \quad \tau_\nu = \int_0^x \varkappa'_\nu \, dx,$$

which differs from solution in diffusion approximation only by the numerical coefficient $\sqrt{3}$ in exponent of the exponential and coefficient $1/\sqrt{3}$ in the relation between flux and density.

Certainly, quantitative distinction for large $\tau_\nu \gg 1$ is huge, but qualitatively the diffusion approximation gives a correct physical result, and for $\tau_\nu \sim 1$ even the numerical error is not so big.

§ 14. Radiation Equilibrium in Stellar Photospheres

Study of distributions of temperature and field of radiation in peripheral layers (photospheres) of stationary stars for the purpose of calculation of luminosity of stars was the classical problem on the basis of which there was built the theory of radiation transfer and developed methods of solution of equation of transfer.*

For us this problem is interesting not only as a classical object for application of theory of transfer of radiation, but also as a model, to which leads, as will be shown in Chapter IX, to some extent, the problem about cooling of a large volume of heated air by means of radiation. Stationary stars are huge gas masses heated to high temperatures, which vary from ten thousand degrees on the surface to millions and tens of millions of degrees in central regions. Mechanical equilibrium of gas is attained due to balancing of forces of pressure, which tend to lead to dispersion of the gas sphere, by gravitational forces which prevent dispersion.

The heated gas sphere — star — radiates from its surface. Loss of energy is replenished by energy release due to nuclear reactions which occur in central regions of the star. Substance in stationary

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*See detailed account of these problems and references to literature in works of V. A. Ambartsumyan [1] and Unsöld [2].

stars is motionless; there is no hydrodynamic motion. Energy released in center is transferred to periphery of star only by radiation and departs into space in the form of radiation. Inasmuch as in peripheral layers there are no nuclear reactions or energy releases, steady state in them is attained due to full compensation of emission and absorption of light in every element of volume: loss of energy of substance by radiation q is equal to zero and temperature at every point is constant in time.*

Equality of emission and absorption of light and absence of losses by radiation are spoken of as radiation equilibrium of star. From condition of radiation equilibrium q = 0, it follows that divergence of radiation flux div S also is equal to zero. Total flux of radiation through spherical surface of any radius r, $4\pi r^2 S$, is constant and is equal to quantity of energy released in center per/unit time ($S \sim 1/r^2$). Distribution of temperature and density of gas over radius of star is determined by means of joint consideration of mechanical equilibrium and radiation transfer. However, in examining of distributions in photosphere, the problem to some extent is divided into two stages. Distribution of temperature over optical coordinate can be found only from consideration of radiation transfer, without knowing distribution of density over radius. Then, in case of necessity, it is possible to go over to distribution of temperature over radius by making use of the conditions of mechanical equilibrium and

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*Steady state of star and invariability of distributions of temperature and other quantities over radius in time does not mean that stars do not evolve. When we speak about steady state in reference to problem about radiation transfer, we consider the invariability of state during a time on the order of the time of heat transfer from center of star to surface.

Let us note that condition of radiation equilibrium q = 0 replaces in a given concrete problem the energy equation of hydrodynamics (2.57).

coefficient of absorption of light as a function of temperature and density.

We will formulate problem about distribution of temperature and radiation transfer in photosphere of star. Since we are interested in surface layers, thickness of which are much less than radius of star, it is possible to disregard their curvature and to consider the photosphere to be flat. Let us direct axis x along outward normal to surface of star (Fig. 2.15), and write equation of radiation transfer for the plane case:

$$\cos\vartheta \frac{dI_\nu}{dx} = \varkappa'_\nu (I_{\nu p} - I_\nu), \tag{2.81}$$

where ϑ is angle between direction of propagation of radiation and the x-axis. To this equation is added condition of radiation equilibrium:

$$q = \int_0^\infty d\nu \int d\Omega \varkappa'_\nu (I_{\nu p} - I_\nu) = c \int_0^\infty d\nu \varkappa'_\nu (U_{\nu p} - U_\nu) = 0, \tag{2.82}$$

and also the boundary condition on the surface, for x = 0, which is that quanta do not arrive from the vacuum:

$$I_\nu (x = 0,\ \vartheta) = 0 \text{ for } \frac{\pi}{2} < \vartheta < \pi. \tag{2.83}$$

If coefficient of absorption of various frequencies $\varkappa_\nu(T, \rho)$ depends on density of gas in identical manner, i.e., if it can be represented in the form $\varkappa_\nu(T, \rho) = \varphi(\nu, T) f(\rho)$, which usually is the case in reality, then by means of introduction in place of x a new coordinate, differential of which is $dy = dx\, f(\rho)$, and which corresponds to optical coordinate, it is possible to exclude from problem the question about distribution of density of gas over x and to look for distribution of temperature and intensity of radiation along this new optical coordinate y. System (2.81)–(2.83) completely describes these distributions. The problem possesses one arbitrary parameter — radiation flux S, which in the plane case is constant ($q = \operatorname{div} S = \frac{dS}{dx} = 0$). Flux S is equal to flow of energy supplied from infinity $x = -\infty$, from within the star, and actually is determined by energy release in center of star. At the same time, flux S constitutes flow of radiant energy going out from surface of star, i.e., integral brightness of surface.

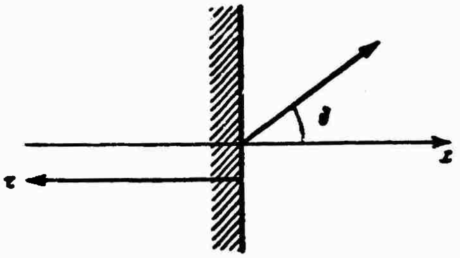

Fig. 2.13. On the problem about radiation transfer in stellar photospheres.

Formulated problem in general presents very large mathematical difficulties. The main one of them is that equation of transfer is written for spectral intensity I_ν, whereas condition of radiation equilibrium has a character which is integral over the spectrum. For simplification of problem we will introduce into consideration a certain coefficient of absorption $\varkappa'$ which is average over the spectrum (which is equivalent to the assumption about "grayness" of the medium) and will integrate equation of transfer (2.81) over the spectrum. We will obtain for integral intensity $I = \int_0^\infty I_\nu \, d\nu$ the equation

$$\cos\vartheta \frac{dI}{dx} = \varkappa'(I_p - I), \quad I_p = \int_0^\infty I_{\nu p} \, d\nu = \frac{cU_p}{4\pi} = \frac{\sigma T^4}{\pi}. \qquad (2.84)$$

Passing over to the optical coordinate, which is measured from surface into depth of photosphere: $d\tau = -\varkappa' dx$, $\tau = -\int_0^x \varkappa' dx$, we will obtain

$$\cos\vartheta \frac{dI}{d\tau} = I - I_p(T). \qquad (2.85)$$

Boundary condition (2.83) now takes the form

$$I(\tau = 0, \vartheta) = 0 \text{ for } \frac{\pi}{2} < \vartheta < \pi. \qquad (2.86)$$

and condition of radiation equilibrium (2.82)

$$\int I\,d\Omega=\int I_p\,d\Omega, \quad U=U_p=\frac{4\sigma T^4}{c}. \tag{2.87}$$

(constant flux S is equal to $S = \int \cos\vartheta\, I\, d\Omega$).

In spite of anisotropy of radiation, integral of intensity over angles, i.e., density of radiation at every point, is equal to equilibrium quantity U_p. More correctly, temperature of substance at every point, which is controlled by radiation transfer, is established in accordance with radiation density at given point $U = U_p$. Even in simplified formulation the problem of solution of system (2.85)–(2.87) (so-called Milne problem) from mathematical point of view is very complicated. Approximate solution of it will be presented in the following paragraph. Now we will derive the integral equation equivalent to this system, which served as a basis for finding of the exact solution.

We will use integral expression for intensity of type (2.32), which in plane case can be written in a form which directly follows from equation (2.85), if we consider it as linear differential equation in I:

$$I(\vartheta,\tau)=\int_{\tau}^{\infty} I_p[T(\tau')]\,e^{-\frac{\tau'-\tau}{\cos\vartheta}}\cdot\frac{d\tau'}{\cos\vartheta} \quad \frac{\pi}{2}>\vartheta>0. \tag{2.88}$$

$$I(\vartheta,\tau)=-\int_{0}^{\tau} I_p[T(\tau')]\,e^{-\frac{\tau'-\tau}{\cos\vartheta}}\,\frac{d\tau'}{\cos\vartheta} \quad \pi>\vartheta>\frac{\pi}{2}. \tag{2.89}$$

First formula gives intensity of radiation propagating in the direction toward the surface. Integration is conducted from $\tau = \infty$, inasmuch as photosphere is assumed to be semi-infinite. Second formula corresponds to radiation going into the depth; thus it is considered that quantum does not arrive from the vacuum.

We will calculate density of radiation $U = \frac{1}{c} \int I \, d\Omega$, using during integration over ϑ from 0 to $\pi/2$ the first formula, and in the interval $\frac{\pi}{2} < \vartheta < \pi$ – the second formula:

$$cU = 2\pi \int_0^{\pi/2} \sin\vartheta \, d\vartheta \int_\tau^\infty I_p e^{-\frac{\tau'-\tau}{\cos\vartheta}} \frac{d\tau'}{\cos\vartheta} - 2\pi \int_{\pi/2}^{\pi} \sin\vartheta \, d\vartheta \int_0^\tau I_p e^{-\frac{\tau'-\tau}{\cos\vartheta}} \frac{d\tau'}{\cos\vartheta}.$$

By changing order of integration, introducing into first integral the new variable $w = 1/\cos\vartheta$, and in the second integral $w = -1/\cos\vartheta$, taking into account the definition of exponential integrals (2.44) and replacing $I_p = cU_p/4\pi$, we will obtain

$$U = \frac{1}{2} \int_\tau^\infty U_p E_1(\tau' - \tau) \, d\tau' + \frac{1}{2} \int_\tau^\tau U_p E_1(\tau - \tau') \, d\tau'. \tag{2.90}$$

Taking into account condition of radiation equilibrium $U = U_p \sim T^4$, we will finally obtain integral equation for equilibrium density U_p or, which is the same, for T^4:

$$U_p(\tau) = \frac{1}{2} \int_0^\infty U_p(\tau') E_1(|\tau' - \tau|) \, d\tau'. \tag{2.91}$$

Let us write out for reference purposes the integral expression for flux in the plane case, which is calculated analogously to density:*

$$S = \frac{c}{2} \int_\tau^\infty U_p E_2(\tau' - \tau) \, d\tau' - \frac{c}{2} \int_0^\tau U_p E_2(\tau - \tau') \, d\tau'. \tag{2.92}$$

From equation (2.91) it is clear that solution $U_p(\tau)$ is determined

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*For point $\tau = 0$ this formula already was obtained above in § 7 (2.45).

It is interesting to compare exact formulas for density and flux in plane case (2.90), (2.92) with those obtained in "forward-backward" approximation (2.73). The latter differ from the first by replacement of exponential integrals by usual ones and also in numerical coefficients.

with accuracy up to the constant factor. This factor corresponds to arbitrary value of flux S.

§ 15. Solution of Problem of Flat Photosphere

Let us find solution of problem formulated in preceding paragraph in the diffusion approximation. After averaging equation of diffusion approximation over spectrum and introducing average coefficient of absorption $\varkappa'$ and mean free path $l' = 1/\varkappa'$, we will write these equations in the form

$$\frac{dS}{dx} = c\varkappa'(U_p - U), \tag{2.93}$$

$$S = -\frac{l'c}{3}\frac{dU}{dx}, \tag{2.94}$$

or, replacing coordinate x by optical thickness τ: $d\tau = -\varkappa' dx$

$$\frac{dS}{d\tau} = c(U - U_p), \tag{2.95}$$

$$S = \frac{c}{3}\frac{dU}{d\tau}. \tag{2.96}$$

Equation (2.95) demonstrates equivalence of conditions of radiation equilibrium $U = U_p$ and constancy of flux S = const. In this case condition of radiation equilibrium leads to strict equivalence of diffusion approximation and approximation of radiant thermal conduction, since due to equality $U = U_p$:

$$S = \frac{c}{3}\frac{dU_p}{d\tau} = \frac{4}{3}\sigma\frac{dT^4}{d\tau}. \tag{2.97}$$

By solving this equation and using boundary condition (2.66) in order to express flux S in terms of temperature of surface T_0:

$$S = 2\sigma T_0^4, \tag{2.98}$$

we will obtain distribution of temperature and density of radiation over optical thickness

$$U=U_p=\frac{4\sigma T^4}{c}=\frac{4\sigma T_0^4}{c}\left(1+\frac{3}{2}\tau\right). \tag{2.99}$$

Effective temperature of surface by definition $S = \sigma T_{ef}^4$ is equal to $T_{ef} = \sqrt[4]{2}\ T_0 \simeq 1.2\ T_0$.

Effective temperature is somewhat higher than true temperature of surface T_0. This is understandable: quanta going out from surface are generated in radiating shell near surface with thickness on the order of mean free path (optical thickness on the order of unity). Temperature of radiating layer is somewhat higher than temperature of surface (Fig. 2.14); therefore "temperature" of outgoing radiation is also somewhat higher. Temperature of medium coincides with effective temperature of radiation at optical depth $\tau = 2/3$. It is possible to say that this depth corresponds approximately to middle of radiating layer.

For problem about radiation equilibrium of photosphere which is considered as "gray material," which reduces to integral equation (2.91), there has been found an exact analytic solution. The problem also has been solved by different methods of approximation, which are more exact than the diffusion approximation. (This problem, which is one of the few problems of theory of transfer of radiation which it is possible to solve exactly, serves usually as the standard for checking different methods of approximation.)

In exact solution, temperature of surface T_0 for the very same flux S, i.e., with the same effective temperature T_{ef}, turns out to be somewhat less than in the diffusion approximation. In exact solution $T_0^4 = \frac{\sqrt{3}}{4} T_{ef}^4$, $T_0 = 0.811\ T_{ef}$, whereas in diffusion approximation $T_0^4 = \frac{1}{2} T_{ef}^4$, $T_0 = 0.841\ T_{ef}$. Distributions of temperature over

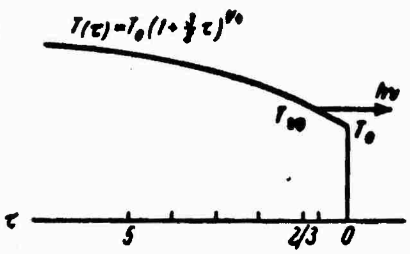

Fig. 2.14. Distribution of temperature over optical coordinate in plane photosphere in the diffusion approximation.

optical thickness in exact and diffusion solutions are very close to one another (they are depicted in Fig. 2.15), which testifies to good accuracy of the diffusion approximation. Error, given by diffusion approximation is less, the greater the optical thickness, i.e., the further from the boundary, which is fully natural. As τ → ∞ exact solution $U_p(\tau)$ asymptotically becomes diffusion solution (2.99). This can be shown directly on the basis of integral expressions for density and flux (2.91), (2.92). This conclusion is useful because it shows how diffusion approximation and approximation of radiant thermal conduction are asymptotically established in the exact equation.

As follows from diffusion solution (2.99), relative change of equilibrium density U_p on mean free path decreases with distance from surface:

$$\frac{\Delta U_p}{U_p} \approx \frac{l}{U_p}\frac{dU_p}{dx} = \frac{1}{U_p}\frac{dU_p}{d\tau} = \frac{1}{\frac{2}{3}+\tau} \approx \frac{1}{\tau}$$

as τ → ∞.

Exponentials integrals E_1 and E_2 rapidly decrease with increase of argument, so that actually in integrals (2.91), (2.92) only region $|\tau' - \tau| \sim 1$ near point τ plays a role.

Therefore, integration over τ' from zero to τ in second integrals in formulas (2.90), (2.92) for τ >> 1 can be extended to -∞, or, which is the same, integration over τ - τ' from zero to τ >> 1 can be extended to interval from 0 to ∞. Error due to this will be less, the larger τ is.

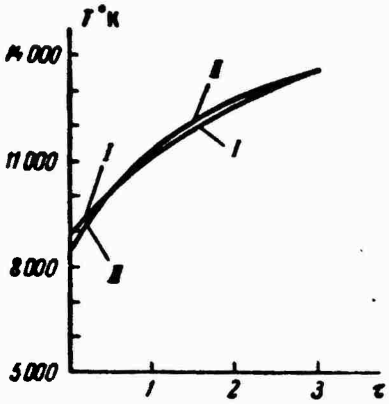

Fig. 2.15. Comparison of distributions of temperature in flat photosphere which are calculated in diffusion approximation (I) and exactly (II). For definiteness effective temperature is selected equal to $T_{ef} = 10,500°K$ (graph is taken from book [I]).

We will expand $U_p(\tau')$ near point τ:

$$U_p(\tau') = U_p(\tau) + \frac{dU_p}{d\tau}(\tau' - \tau) + \frac{1}{2}\frac{d^2U_p}{d\tau^2}(\tau' - \tau)^2 + \ldots$$

Inasmuch as $U_p(\tau')$ is a slow function, as $\tau \to \infty$ higher derivatives of it become less and less. Substituting this expansion in (2.90), (2.91) and calculating integrals, we will obtain from (2.92) with accuracy up to turns which are proportional higher derivatives of U_p up to τ: $S = \frac{c}{3}\frac{dU_p}{d_\tau}$, and from (2.91): $\frac{d^2U_p}{d\tau^2} = 0$, i.e., equations of diffusion approximation and radiant thermal conduction.

The fact that integral density of radiation at every point is equal to equilibrium density corresponding to temperature of substance does not at all mean that the same also pertains to spectral densities.* However, the further from the surface into the depth of the photosphere, the less are the relative changes of temperature at distances on the order of average mean free path, and consequently also mean free paths of various frequencies. Therefore, far from the surface there exists local equilibrium also at every frequency, and by average mean free path $l' = 1/\varkappa'$ we should understand the Rosseland mean. In practice the Rosseland method of averaging can be extended

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*In exactly the same way, from the fact that S = const it does not follow that S_ν = const;

$$\frac{dS_\nu}{dx} = \varkappa'_\nu (U_{\nu p} - U_\nu) \neq 0.$$

to the whole photosphere up to the actual surface. If we know distribution of temperature over average optical thickness and take coefficients of absorption depending on frequency (more exactly, their ratios to the average $\varkappa_{\nu}'/\varkappa'$), it is possible formulas of § 8 to find spectrum of radiation of star (see [1-3]). Spectrum, in general, does not coincide with Planck spectrum corresponding to T_{ef}, but in a number of cases is close to it.

§ 16. Losses of Energy of Heated Body by Radiation

Let us consider losses of energy by radiation of an extire body on the whole. We will consider usual bodies of finite dimensions heated in general nununiformly. Total loss of energy by entire body in 1 sec Q, is obviously equal to the integral of loss of energy of 1 cm^3 in 1 sec over the volume q. Noticing that q = div S, it is possible to write:*

$$Q=\int q\,dV=\int S_0\,d\Sigma, \tag{2.100}$$

where dV is element of volume of body, and $d\Sigma$ is element of surface; S_0 is normal component of radiation flux on surface of body. It is possible to represent it in the form $S_0 = \sigma T_{ef}^4$, where T_{ef} is effective temperature of surface of body.

It is not at all obligatory that effective temperature be close to average temperature of a nonuniformly heated body T. In case of an optically thick body, dimensions x of which are much larger than average mean free path l (we will say, corresponding to average

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*q can change sign over the extent of the body, i.e., individual volumes may be cooled, and others may be heated by radiation.

temperature), flux in order of magnitude is equal to

$$S_0 \sim lc\frac{U_p}{x} \sim \frac{l}{x}\sigma T^4 \ll \sigma T^4; \quad T_{эф} \sim \left(\frac{l}{x}\right)^{\frac{1}{4}} T.$$

For $(l/x)^{1/4} \ll 1$, $T_{ef} \ll T$. Effective temperature is more likely to be near to temperature on the surface. Only in case of a not too thick (optically) bodies can effective temperature be close to average temperature of body (temperature T_{ef} and T can be close together also when in the body, in some special way, there is maintained constant temperature).

Let us consider now optically thin body, dimensions of which are small as compared to certain average mean free path of quanta.*

If optical thickness of body x/l is small, quanta, generated at any point of body almost freely emerge to the outside. Along the path there is absorbed only a fraction of the quanta on the order of $x/l \ll 1$. Density of radiation in the body constitutes a fraction on the order of x/l of equilibrium density, i.e., it is considerably less than equilibrium (radiation is essentially non-equilibrium). Really, intensity of radiation at some point is equal, according to formula (2.32), to the integral over the ray of density of sources within the body. Inasmuch as body is optically thin, $\int_{s'}^{s} \varkappa_\nu' \, ds \sim$ $\sim x''/l_\nu \ll 1$, and exponential factor in the formula, which takes into account absorption of quanta, is close to unity. Then intensity $I_\nu \sim \frac{x}{l_\nu} I_{\nu p}$, and density of radiation after integration over angles $U_\nu \sim \frac{x}{l_\nu} U_{\nu p}$. If we integrate U_ν over spectrum, introducing a certain

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*We designate average mean free path in case of an optically thin body by l_1 in order not to confuse it with Rosseland average mean free path l, which is characteristic for an optically thick body. As we will see below, law of averaging of absorption over spectrum in case of an optically thin body differs from Rosseland law.

average mean free path l_1, we will obtain that $U \sim (x/l_1)\, U_p \ll U_p$. Quantity of energy absorbed in 1 cm^3 in 1 sec also constitutes a fraction on the order of x/l_1 of the energy emitted in 1 cm^3 in 1 sec since both quantities are related as U/U_p, which may be seen from formula for q (2.61).

Thus, in case of an optically thin body, loss of energy by substance in 1 cm^3 in 1 sec reduces, with accuracy up to small quantity of the order of x/l_1, to the emitted energy, i.e., to integral emittance:

$$J = \int_0^\infty J_\nu \, d\nu = c \int_0^\infty \varkappa'_\nu U_{\nu p} \, d\nu. \tag{2.101}$$

If we take mean value of coefficient of absorption, which we will designate by $\varkappa_1$, (equal by definition to reciprocal of average mean free path l_1) outside the integral sign, we will obtain for integral emission:

$$J = \varkappa_1 U_p c = \frac{4\sigma T^4}{l_1}. \tag{2.102}$$

Comparison of formulas (2.102) and (2.101) gives law of averaging of mean free path for case of an optically thin body:

$$\varkappa_1 = \frac{1}{l_1} = \frac{\int_0^\infty \varkappa'_\nu U_{\nu p} \, d\nu}{\int_0^\infty U_{\nu p} \, d\nu} = \int_0^\infty \varkappa'_\nu G_1(u) \, du. \tag{2.103}$$

$$G_1(u) = \frac{15}{\pi^4} \frac{u^3}{e^u - 1}, \quad u = \frac{h\nu}{kT} \tag{2.104}$$

or, in terms of coefficient of true absorption:

$$\varkappa_1 = \frac{1}{l_1} = \int_0^\infty \varkappa_\nu G'_1(u) \, du, \tag{2.105}$$

$$G'_1(u) = (1 - e^{-u})\, G_1(u) = \frac{15}{\pi^4} e^{-u} u^3. \tag{2.106}$$

This method of averaging, as we can see, differs from Rosseland method: during Rosseland averaging by formula (2.77), there is averaged mean free path, i.e., reciprocal of coefficient of absorption, where weighting function is proportional to derivative of Planck function with respect to temperature. Integral emittance is characterized by mean free path, which is obtained by means of averaging the actual coefficient of absorption, with weight proportional to Planck function.

Total loss of energy by a heated optically thin body is determined by integral of emittance over volume:

$$Q=\int q\,dV=\int J\,dV. \tag{2.107}$$

In distinction from an optically thick body, which is cooled by radiation "from the surface," cooling of an optically thin body has essentially a volume character. It is possible, of course, in this case to introduce idea of radiation flux from surface and to write equation (2.107) in form of integral over surface, since formula $q = \operatorname{div} S$ always retains validity. However, in case of volume cooling, such an interpretation of losses has a purely formal character, whereas in case of an optically thick body outgoing quanta in fact are generated in surface shell. In accordance with this, spectrum of radiation of optically thick body in some degree is close to Planck spectrum corresponding to effective temperature T_{ef} or temperature at the surface. Spectrum of radiation of optically thin body can considerably differ from Planck spectrum corresponding to temperature of body, if coefficient of absorption of substance strongly depends on frequency. Spectrum in this case is characterized by frequency function $\varkappa'_{\nu} U_{\nu p}$.

We will compare radiant losses of energy referred to unit of volume of body (rate of cooling of unit of volume) and referred to unit of surface (flux from surface) for cases of optically thick and optically thin bodies. If dimensions of body are on the order of x, its surface is on the order of x^2, and volume is on order of x^3. For optically thick body, rate of cooling referred to surface is on the order of

$$\frac{Q}{x^2} \sim S \sim \frac{l}{x}\sigma T^4 \ll \sigma T^4, \quad \frac{l}{x} \ll 1, \tag{2.108}$$

and rate of cooling referred to volume is

$$\frac{Q}{x^3} \sim \frac{S}{x} \sim \frac{1}{x}\frac{l}{x}\sigma T^4 \sim \left(\frac{l}{x}\right)^2 \frac{\sigma T^4}{l} \ll \frac{\sigma T^4}{l}. \tag{2.109}$$

In case of optically thin body

$$\frac{Q}{x^2} \sim \frac{Jx^3}{x^2} \sim \frac{x}{l_1}\sigma T^4 \ll \sigma T^4; \quad \frac{x}{l_1} \ll 1, \tag{2.110}$$

$$\frac{Q}{x^3} \sim J \sim \frac{\sigma T^4}{l_1}, \quad \frac{x}{l_1} \ll 1. \tag{2.111}$$

Let us compare relative radiant losses of two bodies of approximately identical average temperature, one of which has large dimensions (optically thick), and the other – small dimensions (optically thin). Densities of substance, just as temperatures, will be considered to be close to each other, so that averaged mean free paths l and l_1, which are functions only of temperature and density of substance, are of the same order (difference between methods of averaging over spectrum, as a rule, does not introduce very large numerical differences in magnitudes of mean free paths; l and l_1 usually differ by not more than a few times).

From relationships (2.108) and (2.110) it is clear that in both cases losses referred to surface, i.e., fluxes from the surface, are less than σT^4. Only a body whose dimensions are on the order of mean free path (optical thickness on the order of unity) $x \sim l \sim l_1$, emits from surface radiation flux corresponding to an ideal black body with temperature on the order of average temperature of body.

However, for losses referred to volume, or which is the same, to mass, in case of optically thick body mass rate of cooling is much less than in case of optically thin body, for which it is on the order of average integral emittance $J \sim \sigma T^4/l_1$ over volume and does not depend on dimensions (by virtue of the volume character of radiation).

Physical cause of this is clear: quanta emitted inside optically thick body are "locked" in the body and are not able to emerge to the outside, but are absorbed along their path inside the body.

§ 17. Equations of Hydrodynamics Taking into Account Energy and Pressure of Radiation and Radiant Heat Exchange

In § 9 it was shown how one should take into account the interaction of radiation with substance, which reduces to emission and absorption of light. Then it was assumed that energy and pressure of radiation are small as compared to energy and pressure of the substance.

At very high temperatures or in a strongly rarefied gas (but for large dimensions of the gas body — larger than mean free path of radiation), it is impossible to disregard energy and pressure of radiation. It is quite obvious that in case of local equilibrium of radiation with substance, when $U = U_p = 4\sigma T^4/c$, and radiation pressure $p_\nu = U_p/3 = \frac{4}{3}\sigma T^4/c$, in equations of hydrodynamics it is necessary everywhere to add energy and pressure of radiation to internal energy and pressure of substance, and also to introduce term of radiant thermal conduction. Let us show how this conclusion follows from general equations describing system: substance plus radiation.

In order to write in complete form the equations expressing law of conservation of momentum and energy of system consisting of substance and radiation (in general non-equilibrium), it is convenient to start with divergent form of equations which are equivalent to equations of "continuity" for corresponding quantities. For motion of an ideal gas, without taking into account radiation, these equations were formulated in Chapter I (see formulas (1.7), (1.10)). Equations for system of substance plus radiation are easy to write by means of direct generalization of equations (1.7), (1.10) (let us note that we consider only non-relativistic motions). To momentum density of substance we will add momentum density of radiation $\mathbf{G}$, and to tensor of momentum flux density of substance Π_{ik} we will add tensor of momentum flux density of radiation T_{ik}. As it is known, the last quantity is equivalent to tensor of Maxwellian voltage potentials of an electromagnetic field. In exactly the same way, to energy density of substance we will add energy density of radiation U, and to energy current density we will add energy flux of radiation $\mathbf{S}$, which is Poynting vector (we recall that momentum of radiation if connected with Poynting vector by relationship $\mathbf{G} = \mathbf{S}/c^2$).

We will obtain thus equation of momentum and energy of system

$$\frac{\partial}{\partial t}(\rho u_i + G_i) + \frac{\partial}{\partial x_k}(\Pi_{ik} + T_{ik}) = 0. \qquad (2.112)$$

$$\frac{\partial}{\partial t}\left(\rho\varepsilon + \frac{\rho u^2}{2} + U\right) + \frac{\partial}{\partial x_k}\left\{\rho u_k\left(\varepsilon + \frac{p}{\rho} + \frac{u^2}{2}\right) + S_k\right\} = 0. \qquad (2.113)$$

Equation of continuity remains, obviously, unchanged, since radiation "does not possess" mass,*

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x_k}(\rho u_k) = 0.$$

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*If $U \sim \varepsilon \ll \rho c^2$.

Equations (2.112) and (2.113), which were formulated above by means of simple generalization of equations of hydrodynamics and which have clear physical meaning, can be obtained also by strict formal means, by proceeding from equation of conservation written for four-dimensional energy-momentum tensor of system of mass plus radiation, if in the component of the tensor pertaining to substance we cross over to non-relativistic approximation (we will here not perform this very elementary derivation).

Quantities characterizing radiation and contained in equations (2.112), (2.113) can be interpreted in two ways. In the electromagnetic, field treatment they are expressed in terms of intensities of electrical and magnetic fields **E** and **H**, namely:

$$\left.\begin{aligned} U &= \frac{E^2+H^2}{8\pi}, \\ S &= \frac{c}{4\pi}[EH] = c^2G, \\ T_{ik} &= \frac{1}{4\pi}\left\{-E_iE_k - H_iH_k + \frac{1}{2}\delta_{ik}(E^2+H^2)\right\}. \end{aligned}\right\} \qquad (2.114)$$

It is necessary only to consider that radiation is a rapidly varying electromagnetic field; period of electromagnetic oscillations is insignificantly small as compared to macroscopic times of the process; therefore, it is implied that in the above formulas there is performed averaging over time for a period which is large as compared to period of oscillations of field.

In the quantum treatment, macroscopic quantities U, S, T_{ik} are expressed in terms of distribution function of quanta. If $f(\nu, \mathbf{\Omega}, \mathbf{r}, t)$ is distribution function at point **r** at time t depending upon frequency ν and direction of motion of quanta **Ω**, then, as we already know (see § 1 of this chapter),

$$\left.\begin{aligned} U &= \int h\nu f\, d\Omega\, d\nu, \\ S &= \int h\nu c \Omega f\, d\Omega\, d\nu, \\ T_{ik} &= \int \Omega_i \Omega_k h\nu f\, d\Omega\, d\nu\, ^{*}). \end{aligned}\right\} \qquad (2.115)$$

By means of expansion of rapidly varying electromagnetic fields in Fourier integrals, fields can be represented in the form of superposition of harmonic oscillations of different frequencies. During averaging over time of terms which are quadratic with respect to components of fields and which are contained in formulas for U, S_i, T_{ik}, products of quantities referred to different frequencies disappear, and there remain only quadratic terms with products of Fourier components corresponding to the same frequency. Therefore, energy, momentum, fluxes of energy and momentum of radiation are represented in the form of a linear superposition of terms corresponding to various frequencies. This permits introduction of the idea of intensity of radiation of given frequency $I_\nu(\Omega;\, r,\, t)$ and expression of macroscopic quantities in terms of integrals of intensity over the spectrum and also in terms of directions of propagation of radiation:

$$\left.\begin{aligned} U &= \frac{1}{c} \int I_\nu\, d\Omega\, d\nu, \\ S &= \int \Omega I_\nu\, d\Omega\, d\nu, \\ T_{ik} &= \frac{1}{c} \int \Omega_i \Omega_k I_\nu\, d\Omega\, d\nu, \end{aligned}\right\} \qquad (2.116)$$

It also permits us to cross over to quantum treatment of intensity as the energy of a quantum multiplied by distribution function $I_\nu = h\nu c f$.

It is known that electromagnetic fields, frequencies and directions of propagation of electromagnetic waves, and consequently also

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*Energy of quantum is $h\nu$, momentum is $\Omega h\nu/c$, flux of i-th component of momentum in k-th direction is $\Omega_i\ \Omega_k\ \frac{h\nu}{c}\ c$, whence there is obtained formula for tensor of momentum flux T_{ik}.

integral quantities U, $\mathbf{S}$, T_{ik} depend on what system of coordinates they are measured in.

Integral quantities appearing in equations (2.112) and (2.113) pertain to a "rest," "laboratory" system of coordinates, in which a given particle of substance moves with speed $\mathbf{u}$. Meanwhile parameters of radiation measured in a system of coordinates in which the particle is at rest are more suitable. Really, in state of full thermodynamic equilibrium, energy density of radiation in a substance at rest is equal to the equilibrium quantity $U_p = 4\sigma T^4/c$; radiation flux relative to a motionless substance has a diffusion character, since radiation "drifts" together with the moving substance, and total flux includes this "drift."

Let us cross over in equations (2.112) and (2.113) from quantities U, $\mathbf{S}$, T_{ik} to the primed quantities U', $\mathbf{S}'$, T'_{ik}, which are connected with moving particles of the medium. During motion of medium with non-relativistic velocities $u/c \ll 1$, when it is possible to disregard terms proportional to u/c, the corresponding transformation to a moving system of coordinates gives (see [6]):

$$\left.\begin{aligned} U &= U', \\ S_i &= S'_i + u_i U' + u_k T'_{ik}, \\ T_{ik} &= T'_{ik}. \end{aligned}\right\} \qquad (2.117)$$

Let us introduce the transformed quantities into equations (2.112) and (2.113). Then let us note that momentum of radiation G_i is extraordinarily small as compared to momentum of substance ρu_i, and it can be disregarded.* After writing in explicit form the tensor of

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*If energy of radiation is comparable with energy of substance, i.e., $U \sim \rho u^2$, then momentum of radiation, which is on the order of $G \sim U/c$, is $\frac{c}{u}$ times less than momentum of substance ρu:

$$G \sim \frac{U}{c} \sim \frac{u}{c}\rho u.$$

momentum flux of substance $\Pi_{ik} = \rho u_i u_k + p\delta_{ik}$, we will obtain

$$\frac{\partial}{\partial t}(\varrho u_i) + \frac{\partial}{\partial x_k}(\varrho u_i u_k) + \frac{\partial p}{\partial x_i} + \frac{\partial T'_{ik}}{\partial x_k} = 0, \tag{2.118}$$

$$\frac{\partial}{\partial t}\left(\varrho \varepsilon + \frac{\varrho u^2}{2} + U'\right) + \frac{\partial}{\partial x_k}\left\{\varrho u_k\left(\varepsilon + \frac{p}{\varrho} + \frac{u^2}{2}\right) + S'_k + u_k U' + u_i T'_{ik}\right\} = 0$$

(these equations were obtained by S. Z. Belen'kiy [7])

We will consider the case of local thermodynamic equilibrium of radiation with substance. Density of radiation is equal thus to the equilibrium quantity $U' = 4\sigma T^4/c$. Flux of energy of radiation with respect to substance S'_k is approximately proportional to gradient of equilibrium density of radiation. By formula (2.76) for radiant thermal conduction

$$S'_k = -\frac{lc}{3}\frac{\partial}{\partial x_k}\left(\frac{4\sigma T^4}{c}\right) = -\frac{16\sigma l T^3}{3}\frac{\partial T}{\partial x_k}.$$

Tensor of momentum flux is simplest of all to obtain from formula (2.116) if we note that under conditions of local equilibrium the field of radiation is almost isotropic, and intensity very weakly depends on angle. We will find

$$T'_{ik} = \frac{U'_p}{3}\delta_{ik} = p_\nu \delta_{ik},$$

where $p\nu = \frac{U'p}{3} = \frac{4}{3}\frac{\sigma T^4}{c}$ is radiation pressure.

By substituting all these quantities into equations (2.118), we will find for case of local equilibrium:

$$\frac{\partial}{\partial t}(\varrho u_i) + \frac{\partial}{\partial x_k}(\varrho u_i u_k) + \frac{\partial}{\partial x_i}(p + p_\nu) = 0, \tag{2.119}$$

$$\frac{\partial}{\partial t}\left(\varrho \varepsilon + \frac{\varrho u^2}{2} + U_p\right) + \frac{\partial}{\partial x_k}\left\{u_k\left(\varrho \varepsilon + U_p + \frac{\varrho u^2}{2} + p + p_\nu\right) - \frac{lc}{3}\frac{\partial U_p}{\partial x_k}\right\} = 0, \tag{2.120}$$

where $U_p = 3p_\nu = 4\sigma T^4/c$.

Equations of momentum and energy of system take closed form, since all quantities characterizing radiation are expressed in terms of temperature (and optical properties of substance).

If radiation is not in local thermodynamic equilibrium with substance, then to equations (2.118) it is necessary to add equation of transfer of radiation. About radiation transfer equation of a moving medium, taking into account terms of the order of u/c, see [8].

Literature

1. V. A. Ambartsumyan, E. R. Mustel', A. B. B. Severnyy, and V. V. Sobolev. Theoretical astrophysics. State Technical Press, 1952.

2. A. Unsöld. Physics of stellar atmospheres. IL, 1949.

3. E. R. Mustel'. Stellar atmospheres. Fizmatgiz, 1960.

4. L. Landau and Ye. Lifshits. Statistical physics. State Technical Press, 1951.

5. Yu. P. Rayzer. ZhETF, 32, 1528 (1957).

6. L. D. Landau and Ye. M. Lifshits. Field theory. Fizmatgiz, 1960.

7. S. Z. Belen'kiy. Proceedings of Phys. Inst. of Academy of Sciences of USSR, 10 (1958), p. 15.

8. V. S. Imshchennik and Yu. I. Morozov. PMTF. No. 3, 3, 1963.

CHAPTER III

THERMODYNAMIC PROPERTIES OF GASES AT HIGH TEMPERATURES

1. Gas of Noninteracting Particles

§ 1. Ideal Gas with Constant Heat Capacity and Constant Number of Particles

In many real processes, macroscopic parameters, characterizing state of gas, let us say, density ρ, and specific internal energy ε or temperature T, change quite slowly as compared to rates of relaxation processes leading to establishment of thermodynamic equilibrium. Under such conditions, a particle of gas at every moment of time resides in a state which is very close to the thermodynamically equilibrium state corresponding to instantaneous values of macroscopic parameters. An exception is very fast processes such, for example, as passage of gas through a shock wave front. In this chapter we will consider only thermodynamically equilibrium states of gas.

For description of hydrodynamic motion of substance in adiabatic case, it is necessary to assign entropy or specific internal energy as functions of density and pressure: $S(\rho, p)$, $\varepsilon(\rho, p)$. In nonadiabatic case, usually in equation of energy in explicit form there is contained temperature (for instance, during consideration of thermal conduction or radiation), which it is necessary to relate with density and pressure by means of equation of state $p = p(\rho, T)$.

As it is known, all thermodynamic functions of a substance can be obtained with help of one of generalized thermodynamic potentials, which are given in the form of functions of corresponding variables, namely: $\varepsilon(S, \rho)$; $w(S, p)$; $F(T, \rho)$; $\Phi(T, p)$, where F is free energy, w is enthalpy, and Φ is thermodynamic potential (in the narrow sense).

During concrete calculations of thermodynamic properties of gases, usually there are directly calculated internal energy in dependence upon temperature and density or temperature and pressures $\varepsilon(T, \rho)$ or $\varepsilon(T, p)$. Thus it is necessary to introduce independently equation of state, which it is possible to derive from function $\varepsilon(S, \rho)$, but impossible to find from functions $\varepsilon(T, \rho)$ or $\varepsilon(T, p)$.

Everywhere that this is not specially stipulated, we will consider ideal gases, in which, by definition, it is possible to disregard interaction between particles. In many practically important cases the approximation of idealness is satisfied with great accuracy (non-idealness appears only at sufficiently high densities; see about this in §§ 11-14).

Equation of state of ideal gas can be written in one of the equivalent forms:

$$p = nkT = N\rho kT = \frac{NkT}{V} = \frac{R}{\mu}\rho T = A\rho T, \tag{3.1}$$

where n is number of particles in 1 cm^3, N is number of particles in 1 g, R is universal gas constant,* A is gas constant calculated

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*$R = 8.31 \cdot 10^7$ erg/degree·mole = 1.99 cal/deg·mole, $k = 1.38 \cdot 10^{-16}$ erg/degree = 8.31 joule/degree·mole.

for 1 g, μ is average molecular weight, V is specific volume. Number of particles in 1 g N or average molecular weight μ can themselves depend on temperature and density due to dissociation, chemical reactions or ionization.

Internal energy of gas, and, together with it, heat capacity at constant volume, in general are composed of a series of components, which correspond to different degrees of freedom of gas: translational motion, rotations and vibrations of molecules, electronic excitation of atoms and molecules, and also of components corresponding to dissociation of molecules, process of chemical reactions, ionization. Subsequently, for brevity, we will also include these last factors in the general idea of "degrees of freedom." Just as energy, over degrees of freedom there are summed all the other thermodynamic potentials, and also entropy. Different degrees of freedom, with the exception of translational motion of particles, are included in thermodynamic functions only starting with more or less definite values of temperatures. For degrees of freedom connected with change of number of particles (dissociation, chemical reactions, ionization), these temperatures depend on density of gas.

At very low temperatures, atoms and molecules are not ionized or excited; chemical composition corresponds to the energetically most suitable state; thermal motion is limited to only translational displacements of particles. Specific internal energy, measured from zero temperature, is thus equal to $\varepsilon_{\text{trans}} = \frac{3}{2}NkT$; specific heat capacity at constant volume is $c_{V\ \text{const}} = \frac{3}{2}Nk$.

In a monatomic gas the region of temperatures in which thermodynamic functions are determined purely by translational motion of atoms extends to very high values, on the order of several thousand or even tens of thousands of degrees, until ionization and excitation of electrons in atoms start.

In a molecular gas at the lowest temperatures there are excited rotations of molecules. This occurs usually at several or ten degrees Kelvin. Energies of rotational quanta expressed in degrees (i.e., divided by Boltzmann constant k), are minute: for instance, for oxygen $2.1^{\circ}K$, for nitrogen $2.9^{\circ}K$, for nitric oxide $2.4^{\circ}K$. An exception is only the molecule of hydrogen, for which this magnitude is equal to $85.4^{\circ}K$. Even at room temperature $300^{\circ}K$ (and all the more so at higher temperatures) quantum effects do not play a role. Rotational part of heat capacity is equal to its classical value.

Heat capacity $c_{V\ rot} = Nk$ for diatomic and linear polyatomic molecules and $c_{V\ rot} = \frac{3}{2}Nk$ for nonlinear polyatomic molecules. Corresponding components of internal energy are equal to $\varepsilon_{rot} =$ $= NkT$ or $\frac{3}{2}NkT$.

Vibrations in molecules are excited at much higher temperatures, on the order of several hundred or thousand degrees; therefore there exists a range of temperatures in which thermal motion of molecular gas is composed only of translational and rotational. Heat capacity in this range is constant, and for a diatomic gas (for instance, air) is equal to $c_V = c_{V\ trans} + c_{V\ rot} = \frac{5}{2}Nk$. Corresponding internal energy $\varepsilon = \frac{5}{2}NkT$.

Energies of vibrational quanta expressed in degrees, in diatomic molecules are usually on the order of several thousand degrees. For instance, for O_2 $h\nu/k = 2230^{\circ}K$, for N_2 – $3340^{\circ}K$, for NO – $2690^{\circ}K$; for triatomic molecules the lowest frequency of vibrations is usually less, for instance, for NO_2 $\frac{h\nu}{k} = 916^{\circ}K$, $1960^{\circ}K$, $2310^{\circ}K$. At temperatures which are lower and on the order of $h\nu/k$, vibrational part of heat capacity should be calculated by quantum formulas and itself depends on temperature. However, at temperatures which are higher than $h\nu/k$, vibrational heat capacity is constant and is equal to its classical value k for one vibrational degree of freedom. Diatomic molecule has one vibrational degree of freedom, nonlinear m-atomic molecule has 3m-6, and linear molecule has 3m-5 degrees of freedom.

Thus, at temperatures higher than the largest of values of $h\nu/k$, total classical heat capacity from calculation for one molecule $c_V = c_{V\ trans} + c_{V\ rot} + c_{V\ vib}$ is equal to $c_V = \frac{3}{2}Nk + Nk + (3m - 5)Nk = (3m - \frac{5}{2})Nk$ for linear m-atomic molecules and $c_V = \frac{3}{2}Nk + \frac{3}{2}Nk + (3m - 6)Nk = (3m - 2)Nk$ for nonlinear molecules. For diatomic molecules $c_V = \frac{7}{2}Nk$. Equation of adiabat for ideal gas with constant heat capacity and constant number of particles is determined from general thermodynamic relationship:

$$T\,dS = d\varepsilon + p\,dV = c_V\,dT + NkT\frac{dV}{V} = 0.$$

Hence there is obtained after integration

$$T \sim V^{-(\gamma-1)} \sim \rho^{\gamma-1}; \quad p \sim V^{-\gamma} \sim \rho^{\gamma}, \tag{3.2}$$

where proportionality factors depend only on entropy. Here $\gamma = c_p/c_V$ is adiabatic index; $c_p = c_V + Nk$ is specific heat capacity at constant pressure. For instance, for monatomic gas $\gamma = \frac{5}{3}$, for diatomic gas with unexcited vibrations — $\gamma = \frac{7}{5}$; with completely excited vibrations — $\gamma = \frac{9}{7}$.

It is necessary, however, to note that there does not exist a wide range of temperatures in which vibration in molecules would be completely excited, and heat capacity and adiabatic index would be constant, since dissociation of molecules and chemical reactions frequently start at such temperatures, when the vibrational part of heat capacity only attains its limiting classical value.

§ 2. Calculations of Thermodynamic Functions by Method of Statistical Sums

In the most rigorous and systematic way, all thermodynamic functions can be found with help of so-called method of statistical sums. Let us expound briefly basis of this method* in order to obtain expression for entropy, quantum formula for vibrational energy of molecule, and also in order to apply it in the subsequent sections to a gas with variable number of particles.

According to statistical mechanics, probability of n-th state of system, consisting of N particles, energy of which is equal to E_n, is proportional to the quantity exp $(-E_n/kT)$. Sum of these probabilities over all possible states of system and determined with accuracy up to the constant factor

$$Q=\sum_n e^{-\frac{E_n}{kT}}, \tag{3.3}$$

is called statistical sum of system.

For ideal Boltzmann gas consisting of molecules of several types, numbers of which are equal to N_A, N_B,. . . , statistical sum is expanded into the product of factors corresponding to every type of particle:

$$Q=\frac{Z_A^{N_A}}{N_A!}\cdot\frac{Z_B^{N_B}}{N_B!}\cdots \tag{3.4}$$

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*Detailed derivations can be found in courses of statistical physics, for instance, in book of L. D. Landau and E. M. Lifshits [1].

Here Z_A, Z_B, . . . are statistical sums of one molecule of every type, which are expressed by formulas similar in form to (3.3):

$$Z=\sum_k e^{-\frac{\varepsilon_k}{kT}}, \tag{3.5}$$

where ε_k is energy of molecule in k-th state, and summation is produced over all possible states of one molecule.

General formula for free energy of system has the form

$$F=-kT\ln Q. \tag{3.6}$$

If we replace factorials in expression (3.4) by the formula of Stirling $N! \approx (N/e)^N$ and place obtained expression in (3.6), we will obtain

$$F=-N_A kT\ln\frac{Z_A e}{N_A}-N_B kT\ln\frac{Z_B e}{N_B}-\ldots \tag{3.7}$$

Inasmuch as free energy is thermodynamic potential with respect to the variables: temperature and density (volume), all thermodynamic functions can be derived from formula (3.7) if there are known statistical sums of molecules in dependence upon temperature T and volume V. By general formulas of thermodynamics, entropy, internal energy and pressure are equal to

$$S=-\left(\frac{\partial F}{\partial T}\right)_{VN}, \tag{3.8}$$

$$\varepsilon=F+TS=-T^2\frac{\partial}{\partial T}\left(\frac{F}{T}\right)_{V,N}{}^{*)}, \tag{3.9}$$

$$p=-\left(\frac{\partial F}{\partial V}\right)_{T,N}. \tag{3.10}$$

If we disregard interaction between electronic states, vibrations and rotations, consider molecule as a rigid rotator, and consider vibrations to be harmonic, energy of molecule can be

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*As it is easy to check by means of direct substitution of (3.6), (3.3) in (3.9) $\varepsilon = \Sigma E_n \exp(-E_n/kT)/\Sigma\exp(-E_n/kT)$, internal energy is simply energy of system averaged over all possible states.

represented in the form of sum of energies corresponding to different degrees of freedom. Thus, as one may see from formula (3.5), statistical sum of one molecule also is expanded into the product:

$$Z = Z_{\text{пост}} \cdot Z_{\text{вращ}} \cdot Z_{\text{кол}} \cdot Z_{\text{эл}}. \qquad (3.11)$$

We will give here formula for statistical sums without derivation.

Translational statistical sum of any particle is equal to

$$Z_{\text{пост}} = \left(\frac{2\pi MkT}{h^2}\right)^{\frac{3}{2}} V, \qquad (3.12)$$

where M is mass of particle, and V is volume, occupied by gas (if by N we understand number of particles in 1 g, then V is specific volume).

Rotational sum at temperatures much higher than energy of rotational quantum divided by k is equal to

$$Z_{\text{вращ}} = \frac{8\pi^2 IkT}{h^2} \cdot \frac{1}{\sigma} \qquad (3.13)$$

for a diatomic or linear polyatomic molecule* and

$$Z_{\text{вращ}} = \frac{8\pi^2}{\sigma} \cdot \left(\frac{2\pi IkT}{h^2}\right)^{\frac{3}{2}} \qquad (3.14)$$

for a nonlinear polyatomic molecule.

Here I in the first of the formulas is moment of inertia of linear molecule, and in the second is geometric mean of three moments of inertia of nonlinear polyatomic molecule $I = (I_1 I_2 I_3)^{1/3}$; σ is so-called symmetry factor, which is equal to the number of permutations of identical atoms in the molecule, which are equivalent

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*Energy of rotational quantum $h\nu_{\text{rot}} = h^2/8\pi^2 I$, so that $Z_{\text{rot}} = kT/h\nu_{\text{rot}} \cdot \sigma$.

to rotation of the molecule as a whole increased by one.*

Quantum expression for statistical sum of harmonic oscillator of frequency ν is:

$$Z_{кол} = (1 - e^{-\frac{h\nu}{kT}})^{-1}. \tag{3.15}$$

In this formula energy of oscillations is measured from the lowest quantum vibrational level. It is assumed that energy of zero-point vibrations $h\nu/2$ is included in energy of ground state of molecule.

If molecule possesses several vibrational degrees of freedom, then its total vibrational sum is represented in the form of product of factors corresponding to all normal vibrations.

Finally, electronic statistical sum retains its initial form:

$$Z_{эл} = \sum_{n} e^{-\frac{\varepsilon_n}{kT}}, \tag{3.16}$$

where ε_n is energy of n-th electronic quantum state of atom or molecule. If levels are degenerate, then every component all the same is contained in sum in the form of an independent term, so that numbers of identical terms are equal to statistical weights of levels.

Different atomic and molecular constants necessary for calculation of thermodynamic functions of gases are known usually from spectroscopic data. Energies rotational and vibrational quanta for a series of molecules already have been given in the preceding section. Energies of first excited electronic states of atoms and molecules ε_1 usually are on the order of several ev, i.e., ε_1/k is on the

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*For instance, in diatomic molecule consisting of identical atoms, $\sigma = 2$, and of different atoms, $\sigma = 1$.

order of several tens of thousands of degrees; for instance, for atoms of O ^1D-term $\varepsilon_1 = 1.96$ ev, $\varepsilon_1/k = 22{,}800^\circ K$; for N $^2D^o$-term $\varepsilon_1 = 2.37$ ev, $\varepsilon_1/k = 27{,}500^\circ K$; for the molecules: N_2 — $A^3\Sigma_u^+$-term $\varepsilon_1 = 6.1$ ev, $\varepsilon_1/k = 71{,}000^\circ K$; for NO — $A^2\Sigma^+$-term $\varepsilon_1 = 5.29$ ev, $\varepsilon_1/k = 61{,}400^\circ K$. The occur exceptions: Thus, for a molecule of O_2, the first excited levels are low — $^1\Delta_g$-term $\varepsilon_1 = 0.98$ ev, $\varepsilon_1/k = 11{,}300^\circ K$; $^1\Sigma_g^+$-term, $\varepsilon_2 = 1.62$ ev, $\varepsilon_2/k = 18{,}800^\circ K$.

At not too high temperatures, when $T \ll \varepsilon_1/k$, electronic sum reduces essentially to terms corresponding to ground electronic state. If intervals between levels of fine structure of ground state (when such exists) are less than kT,* then corresponding terms in Z_{el} can be approximately considered to be identical. By measuring energy ε_n from ground state ($\varepsilon_0 = 0$), it is possible to assume that Z_{el} is equal to statistical weight of ground state g_0 (for instance, for atoms: O ^3P-term $g_0 = 9$; for N (^4S) $g_0 = 4$; for molecules; O_2 ($^3\Sigma$) $g_0 = 3$; N_2 ($^1\Sigma$) $g_0 = 1$; NO ($^2\Pi$) $g_0 = 4$).

Calculation of Z_{el} at high temperatures will be discussed in § 6.

Inasmuch as statistical sum of molecule Z is equal to product of separate factors corresponding to different degrees of freedom, free energy of gas, and together with it other thermodynamic functions, are represented in the form of sum of corresponding terms. Putting expression for factors of Z in formula (3.7), we will obtain explicit expression of free energy in terms of temperature and density;

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*For instance, for atom O, intervals for components of fundamental triplet state $^3D_2$ are equal to $\Delta\varepsilon/k = 230^\circ$ and $320^\circ K$; for NO, splitting of doublet $^2\Pi$ — $\Delta\varepsilon/k = 178^\circ K$. For spectroscopic symbolism and interpretation of designations of terms see § 14 Chap. V.

the latter is contained due to the fact that translational sums Z_{trans} contain volume V. Quantities N_A/V, N_B/V, . . . , which appear under the sign of logarithm in formula (3.7), are numbers of particles per unit of volume n_A, n_B, . . . , which are expressible in terms of density of gas and percentage contents of particles of various types, which in this case are constant.

Statistical sum of monatomic gas consists only of translational and electronic factors; putting it in (3.7), we will find free energy of N identical atoms (we consider $Z_{el} = g_0$):

$$F = -NkT \ln \left(\frac{2\pi MkT}{h^2}\right)^{\frac{3}{2}} \frac{eVg_0}{N}. \tag{3.17}$$

Specific entropy of monatomic gas in absence of ionization and excitation of electrons, by formula (3.8) is equal to

$$S = Nk \ln \frac{e^{\frac{5}{2}} g_0}{n} \left(\frac{2\pi MkT}{h^2}\right)^{\frac{3}{2}}. \tag{3.18}$$

For energy and pressure we obtain the already known expressions:

$$\varepsilon = \frac{3}{2} NkT, \quad p = nkT.$$

In an analogous way it is easy to obtain rotational and vibrational components of thermodynamic functions. Internal energy of rotations, naturally, coincides with formulas, written in § 1, and internal energy of vibrations is expressed by Planck function. Energy of N identical oscillators (diatomic molecules) is equal to

$$\varepsilon_{\text{кол}} = N \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1}. \tag{3.19}$$

In the limit $kT \gg h\nu$ it tends to its classical value $\varepsilon_{vib} = NkT$, and heat capacity $c_{V\ vib} = \frac{\partial \varepsilon_{vib}}{\partial T} \rightarrow Nk$. Actually, energy and heat capacity are close to their limiting values already at $kT \approx h\nu$. For instance, for $kT/h\nu = 0.5$, $c_V/Nk = 0.724$; for $kT/h\nu = 1$, $c_V/Nk = 0.928$; for $kT/h\nu = 2$, $c_V/Nk = 0.979$.

Rotations and vibrations of molecules give no contribution to pressure. Formally this is connected with the fact that corresponding statistical sums, and also internal energies and heat capacities do not depend on volume. Pressure of an ideal gas is connected exclusively with translational motion of particles.

At high temperatures on the order of several thousand degrees, when amplitudes of vibrations of molecules become considerable as compared to interatomic distances, there appear anharmonicity of vibrations and interaction of vibrations with rotations. Anharmonicity somewhat decreases vibrational part of heat capacity. Corresponding corrections in first approximation are proportional to temperature. Usually these corrections are small (dissociation of molecules starts before the corrections become large). For calculation of corrections see, for instance, [2].

§ 3. Dissociation of Diatomic Molecules

At temperatures on the order of several thousand degrees, diatomic molecules usually dissociate into atoms. Polyatomic molecules, in which bond is weaker, start to disintegrate at lower temperatures. Breaking-up of molecule requires very great expenditure of energy; therefore dissociation considerably affects thermodynamic functions of gas.

Let us consider the simple and at the same time practically important case of a diatomic gas of molecules of one sort A_2, consisting of identical atoms A. Let us assume that at temperature

T and density of ρ there is dissociated into atoms fraction α of initial molecules (according to the scheme $A_2 \rightleftarrows 2A$). If N is number of initial molecules in 1 g, then at degree of dissociation α in 1 g there are contained $N \cdot 2\alpha$ atoms and $N(1 - \alpha)$ molecules; total number of particles is equal to $N(1 + \alpha)$, so that pressure of gas

$$p = N(1+\alpha)\varrho kT. \tag{3.20}$$

For complete dissociation ($\alpha = 1$) it is twice as large as pressure at the same T, and ρ, but in the absence of dissociation.

For small dissociation $\alpha \ll 1$, change of pressure is small, but change of energy and heat capacity of gas all the same can be considerable. Let us assume that ε_{A_2} is energy of one molecule at temperature T, and ε_A is energy of one atom. Let us designate energy necessary for breaking-up of unexcited molecule (i.e., in reference of rotations and vibrations or at T = 0) by U. U is binding energy or energy of dissociation of molecule; for instance, for O_2: U = 5.11 ev → 118 kilocalories/mole,* U/k = 59,400°K; N_2: U = 9.74 ev → 225 kilocalories/mole, U/k = 113,000°K; NO: U = 6.5 ev → 150 kilocalories/mole, U/k = 75,500°K.

Specific internal energy of gas measured from molecular state at zero temperature is equal to

$$\varepsilon = N\varepsilon_{A_2}(1-\alpha) + N \cdot \varepsilon_A \cdot 2\alpha + NU\alpha. \tag{3.21}$$

Usually dissociation starts at temperatures much lower than U/k lower, the more rarefied the gas is. At density of atmospheric air ($n = 2.67 \cdot 10^{19}$ molecules/cm^3), dissociation is noticeable already at $kT/U \sim 1/20$. This is connected with large statistical weight of state in which molecule is broken up into atoms. Actually, at

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*1 ev/molecule corresponds to 23.05 kilocalories/mole.

$kT \ll U$, molecules are broken up by impacts with very energetic particles, which belong to the extreme tail of the Boltzmann energy distribution. In absence of ionization and electronic excitation $\varepsilon_A = \frac{3}{2}kT$. If kT is larger than energy of vibrational quanta $h\nu$, vibrational energy of molecule, as follows from formula (3.19), is equal approximately to kT and $\varepsilon_{A_2} \approx \frac{7}{2}kT$. Energy of dissociated gas (3.21) noticeably exceeds energy in absence of dissociation $\varepsilon = N\varepsilon_{A_2}$, even at small degrees of dissociation ($\alpha \sim 0.1$ and less), due to the last term, which corresponds to energy expended to break up molecules. In exactly the same way, heat capacity $c_V = \left(\frac{\partial \varepsilon}{\partial T}\right)_V$ of dissociating gas noticeably increases.

It is necessary to note that formulas (3.20), (3.21) are also valid under conditions of non-equilibrium dissociation, when degree of dissociation differs from its thermodynamic equilibrium value, which corresponds to "temperature" and density of gas. By "temperature" here is implied temperature of translational and rotational degrees of freedom of particles, which are always thermodynamic equilibrium.*

Thermodynamic equilibrium degree of dissociation is uniquely determined by temperature and density (or pressure) of gas. Dependence of degree of dissociation on temperature and density can be derived from general expression for free energy of gas which is a mixture of particles of various types (3.7), if we consider that to the equilibrium composition of the mixture undergoing

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*Equilibrium in vibrational degrees of freedom is established more slowly than in rotational and translational, but usually faster than equilibrium dissociation is established. For detail about this see Chap. VI.

chemical transformations, the particular case of which is dissociation, there should correspond the minimum of free energy.

Let us consider free energy F as a function of number of particles N_{A_2} and N_A at given temperature, volume, and initial number of molecules $N^0_{A_2}$:

$$F = -N_{A_2}kT \ln \frac{Z_{A_2}e}{N_{A_2}} - N_A kT \ln \frac{Z_A e}{N_A}.$$

We will form the variation δF:

$$\delta F = -\delta N_{A_2}\left(kT \ln \frac{Z_{A_2}e}{N_{A_2}} - kT\right) - \delta N_A \left(kT \ln \frac{Z_A e}{N_A} - kT\right)^*$$

Variations δN_{A_2} and δN_A are related to each other by the condition of conservation of number of atoms

$$N_{A_2} + \frac{N_A}{2} = N^0_{A_2} = \text{const}; \quad \delta N_{A_2} = -\frac{1}{2}\delta N_A.$$

By equating δF to zero (minimum of free energy) under the condition of conservation of number of atoms, we will obtain

$$\frac{N_A^2}{N_{A_2}} = \frac{Z_A^2}{Z_{A_2}}. \qquad (3.22)$$

Inasmuch as statistical sums Z_A and Z_{A_2} are proportional to volume V, which is contained in translational sums, and in other respects depend only on temperature, instead of (3.22) it is possible to write

$$\frac{n_A^2}{n_{A_2}} = f(T), \qquad (3.23)$$

or, for partial pressures $p_i = n_i kT$:

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*Quantities in parentheses constitute chemical potentials of molecules and atoms, taken with reverse sign:

$$\mu_{A_2} = \frac{\partial F}{\partial N_{A_2}}, \quad \mu_A = \frac{\partial F}{\partial N_A}.$$

$$\frac{p_A^2}{p_{A_2}} = f(T)\cdot kT = K_p(T). \tag{3.24}$$

Expressions (3.22) or (3.23), (3.24) are a particular case of so-called law of mass action for chemical equilibrium, and quantity $K_p(T)$ is called equilibrium constant for dissociation reaction. It depends only on temperature and molecular (and atomic) constants. Putting in (3.22) the expressions for statistical sums of molecules A_2 and atoms A and considering for simplicity that vibrations in molecules are completely excited, i.e., $Z_{vib} \approx kT/h\nu$ (see formula (3.15)), and in electronic statistical sums there participate only terms corresponding to ground states of molecule and atom, we will obtain

$$\frac{p_A^2}{p_{A_2}} = K_p(T) = \frac{M_A^{\frac{3}{2}}\nu\sqrt{kT}}{4\pi^{\frac{1}{2}} I_{A_2}} \frac{g_{0A}^2}{g_{0A_2}} \cdot e^{-\frac{U}{kT}}. \tag{3.25}$$

The last two factors in (3.25) appeared from quotient of electron statistical sums:

$$\frac{Z_{el\,A}^2}{Z_{el\,A_2}} \approx \frac{g_{0A}^2}{g_{0A_2}} e^{-\frac{(2\varepsilon_{0A}-\varepsilon_{0A_2})}{kT}} = \frac{g_{0A}^2}{g_{0A_2}} e^{-\frac{U}{kT}},$$

since difference between zero-point energies $2\varepsilon_{0A} - \varepsilon_{0A_2}$, by definition, is equal to energy of dissociation U.

Passing in (3.25) from partial pressures to degree of dissociation,

$$\alpha = \frac{N_{A_2}^0 - N_{A_2}}{N_{A_2}^0} = \frac{N_A}{2N_{A_2}^0},$$

we will obtain

$$\frac{\alpha^2}{1-\alpha} = \frac{1}{4n_{A_2}^0}\cdot\frac{K_p(T)}{kT} = \frac{M_A^{\frac{3}{2}}\nu}{16\pi^{\frac{1}{2}} I_{A_2}\sqrt{kT}} \cdot \frac{g_{0A}^2}{g_{0A_2}} \cdot \frac{1}{n_{A_2}^0} e^{-\frac{U}{kT}}, \tag{3.26}$$

where $n^0_{A_2} = \rho/M_{A_2}$ is number of initial molecules in 1 cm^3 of gas.

For small degrees of dissociation $\alpha \approx 1$ (when $U/kT \gg 1$), as can be seen from formula (3.26), $\alpha \sim \rho^{-1/2}e^{-U/2kT}$, i.e., α sharply increases with increase of temperature and slowly increases during rarefaction of gas. Fast increase of degree of dissociation with increase of temperature entails sharp increase of heat capacity. At high temperatures, when dissociation is almost complete, $\alpha \approx 1$, concentration of molecules $1 - \alpha \sim \rho e^{U/kT}$ is proportional to density and changes more slowly with temperature, since U/kT now is not a very large number.

It would seem that at high temperatures, after termination of dissociation, heat capacity of gas (which was converted to a monatomic gas) should decrease and become equal to 3/2 k per atom or 3 k per initial molecule, i.e., even less than before dissociation (7/2 k per molecule). In reality, this usually does not occur, since after termination of dissociation with increase of temperature (and sometimes even before termination), there starts ionization of atoms (and molecules), which introduces its own (considerable) contribution to heat capacity.

Dependence of degree of dissociation on temperature and density of gas, and also influence of dissociation on thermodynamic functions are illustrated in Tables 3.1 and 3.2, which are composed according to tables of [3], in which there are given corresponding values for air (79% N_2 + 21% O_2) in region of dissociation.*

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*In Table 3.2, data of [3] pertain only to temperatures lower than 20,000°K. Higher temperatures are considered in work [4] (see below).

Reaction of oxidation of nitrogen $N_2 + O_2 \rightleftarrows 2NO$, which occurs in air (see following section), does not strongly affect dissociation of molecules of N_2 and O_2 and thermodynamic functions of air.

Table 3.1. Equilibrium Composition of Air in Region of Dissociation and Beginning of Ionization

Normal density $\rho_0 = 1.29 \cdot 10^{-3}$ g/cm^3

T °K	N_2	N	O_2	O	NO	N^+	O^+	NO^+
2000	0,788		0,205	0,015	0,007			
4000	0,749	0,0004	0,100	0,134	0,084			
6000	0,744	0,044	0,006	0,356	0,050			
8000	0,571	0,416	0,007	0,393	0,024			
10 000	0,222	1,124		0,407	0,009	0,0034		0,0015
12 000	0,050	1,458		0,411	0,003	0,020	0,0034	0,001
15 000	0,006					0,096	0,015	

Density $\rho = 10^{-2}\rho_0$

T °K	N_2	N	O_2	O	NO	N^+	O^+	NO^+
2000	0,788		0,248	0,002	0,007			
4000	0,777	0,004	0,008	0,378	0,024			
6000	0,592	0,394		0,413	0,005			
8000	0,068	1,440		0,416	0,001	0,004	0,001	0,0001
10 000	0,004	1,528		0,410		0,046	0,008	0,0002
12 000		1,380		0,384		0,202	0,034	
15 000		0,858		0,282		0,724	0,136	

Concentrations of all particles c_i here are defined as ratio of number of particles of given type to initial number of molecules. At room temperature $c_{N_2} = 0.791$, $c_{O_2} = 0.209$. Data for argon are not given, since its role is very small.

The latter are mainly determined by dissociation of N_2, O_2, so that effects of dissociation and all dependences are seen from Table 3.2. For comparison, in the table there are shown values of energies corresponding to given temperatures on the assumption that dissociation is absent (specific energy in this case does not dpend on density). Inasmuch as ionization starts before dissociation

Table 3.2. Thermodynamic Functions of Air

Normal density $\rho_0 = 1.29 \times 10^{-3}$ g/cm^3

T °K	ε, $\frac{ev}{molecule}$	P, atm	γ	$\frac{7}{2}kT$, ev/molecule
2000	0,515	7,42	1,335	0,604
4000	1,52	15,8	1,240	1,21
8000	5,38	41,7	1,180	2,42
12 000	12,7	88	1,160	3,92
20 000	24	183	1,175	6,04
50 000	95	870	1,215	15,1
100 000	276	2690	1,225	30,2
250 000	922	10870	1,275	75,4
500 000	1450	23150	1,370	151

Density $\rho = 10^{-2}\rho_0$

T °K	ε, $\frac{ev}{molecule}$	P, atm	γ
2000	0,520	0,074	1,330
4000	2,09	0,177	1,195
8000	10,6	0,575	1,125
12 000	16,6	0,994	1,140
20 000	45,3	2,8	1,145
50 000	158	11,6	1,170
100 000	499	37,3	1,175
250 000	1080	125	1,270
500 000	3310	412	1,290

Internal energies are given in electron volts per initial molecule; for air, 1 ev/molecule = 0.8 kilocalories/g. Effective adiabatic index γ is defined as $\gamma = 1 + \frac{P}{\rho\varepsilon}$. In the last column, for comparison, there is given energy $\varepsilon = \frac{7}{2}kT \frac{ev}{molecule}$, which air would possess in absence of processes of dissociation and ionization, but with classical vibrations of molecules.

of nitrogen is finished, in the table are also shown concentrations of ions (for ionization see § 5). It is necessary to note that during exact calculations of dissociation and thermodynamic functions, there are used not simple formulas of type (3.26), but more exact ones, taking into account excitation of highest electronic states, anharmonicity of vibrations, etc.

Thus we start with exact expressions (3.22), calculating statistical sums on the basis of spectroscopic data on atoms and molecules. Description of method of such calculations can be found in work [5].

§ 4. Chemical Reactions

Chemical composition of mixture of gases under ordinary conditions, i.e., at room temperature, very frequently differs from thermodynamic equilibrium composition. This is connected with the fact that for occurrence of chemical reaction, even if there is then liberated heat and the gas passes into an energetically more favorable state, usually there is required activation energy E. Chemical reaction rate, which is proportional to Boltzmann factor $e^{-E/kT}$, at low temperatures and high activation energies, when $E/kT \gg 1$, is very low and reaction practically does not occur. Thus, system of mixture of gases is in equilibrium, but this is not thermodynamic equilibrium. Such equilibrium can be called conditional. As a typical example can serve a mixture of hydrogen and oxygen in composition $H_2 + \frac{1}{2} O_2$, which under conditions of thermodynamic equilibrium at low temperatures would have to completely be turned into water H_2O (energy of reaction is 57.1 kilocalories/mole). However, at usual temperatures and without influence of external factors, this irreversible reaction does not occur, and mixture is in state of conditional equilibrium.

At high temperatures on the order of several thousand degrees (for certain reactions at lower temperatures), rate of chemical transformations are high, and in mixture of gases there is established chemical equilibrium. Flow of reversible reactions (i.e., reactions which can occur in both directions, in accordance with condition of chemical equilibrium at given temperature and density) affects chemical composition and thermodynamic functions of gases. An example is air, in which at high temperatures on the order of several thousand degrees there occurs oxidation of part of nitrogen by the scheme:

$$\frac{1}{2}N_2+\frac{1}{2}O_2+21{,}4\ \frac{\text{kcal}}{\text{mole}}\rightleftarrows NO. \tag{3.27}$$

Reaction of oxidation of nitrogen requires high activation energy, so that at temperatures below ~1500°K it practically does not occur (for achievement of equilibrium there are necessary very long times); however, at temperatures ~3000°K and above, equilibrium is established very quickly (at normal air density in 10^{-4} sec and less), and it is possible to speak about equilibrium composition of air, taking into account formation of nitric oxide.*

Let us consider chemical equilibrium and influence of it on thermodynamic properties of mixture of gases in the example of a reaction of the type of oxidation of nitrogen, i.e., of the type

$$A_2+B_2\rightleftarrows 2AB. \tag{3.28}$$

Let us assume for simplicity that dissociation of molecules is small. This assumption is justified at not too high temperatures; for instance, in air at T ~ 2000-3000°K dissociation of molecules N_2, O_2 is very small, and equilibrium concentration of nitric oxide is noticeable.

Let us assume that in one gram of initial mixture there are contained $N^0_{A_2}$ and $N^0_{B_2}$ molecules A_2 and B_2; concentrations of them are $m^0_{A_2} = N^0_{A_2}/N$ and $m^0_{B_2} = N^0_{B_2}/N$, where $N = N^0_{A_2} + N^0_{B_2}$ is total number of molecules in 1 g of initial gas. Let us assume that at temperature T and density of gas ρ equilibrium numbers of molecules in 1 g are equal to N_{A_2}, N_{B_2}, N_{AB}, and concentrations

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*For detail about rates of reaction of oxidation of nitrogen, see Chapter VI, § 8, and about kinetics of reaction in a shock wave, see Chap. VIII, § 5.

$m_i = N_i/N$ are equal to m_{A_2}, m_{B_2}, m_{AB}. Numbers of molecules and concentrations are related with each other by conditions of conservation of number of atoms:

$$N_{A_2}+\frac{1}{2}N_{AB}=N^0_{A_2},\quad N_{B_2}+\frac{1}{2}N_{AB}=N^0_{B_2}, \tag{3.29}$$

$$m_{A_2}+\frac{1}{2}m_{AB}=m^0_{A_2},\quad m_{B_2}+\frac{1}{2}m_{AB}=m^0_{B_2}. \tag{3.30}$$

Let us designate by ε_{A_2}, ε_{B_2}, ε_{AB} energies of one molecule, and by $2U'$, the energy of reaction, i.e., energy which is released during transformation of the two molecules, A_2 and B_2, into two molecules AB (if reaction occurs with absorption of heat, $U' < 0$).

Then, if as before we take as zero energy the energy of initial mixture $A_2 + B_2$ at $T = 0$, we will obtain that specific internal energy of gas is equal to

$$\varepsilon = Nm_{A_2}\varepsilon_{A_2}+Nm_{B_2}\varepsilon_{B_2}+Nm_{AB}\varepsilon_{AB}-Nm_{AB}U'. \tag{3.31}$$

Total number of particles in gas during considered reaction does not change, so that pressure at these same T and ρ is not influenced by the reaction.*

Numbers of particles participating in reaction are related with each other under conditions of equilibrium by law of mass action, which it is possible to derive from general expression for free energy fully analogously to the way this was done in case of dissociation of molecules. For this we seek minimum of free energy for constant T, ρ and numbers of initial molecules $N^0_{A_2}$ $N^0_{B_2}$, but variable N_{A_2}, N_{B_2}, N_{AB}.

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*Just as for dissociation, formula (3.31) is accurate in the case when chemical equilibrium is absent and concentrations are non-equilibrium.

As a result we will obtain

$$\frac{N_{AB}^2}{N_{A_2}N_{B_2}}=\frac{Z_{AB}^2}{Z_{A_2}\cdot Z_{B_2}} \qquad (3.32)$$

in full analogy with formula (3.22) for dissociation.

By factoring out volumes from translational statistical sums, we will obtain for numbers of particles in 1 cm^3 or partial pressures:

$$\frac{n_{AB}^2}{n_{A_2}n_{B_2}}=\frac{p_{AB}^2}{p_{A_2}p_{B_2}}=K_p'(T), \qquad (3.33)$$

where $K_p'(T)$ is equilibrium constant for reaction (3.28). By substituting expressions for statistical sums, as in the case of dissociation, we will obtain

$$K_p'(T)=4\left(\frac{M_{AB}}{M_{A_2}M_{B_2}}\right)^{\frac{3}{2}}\frac{I_{AB}^2}{I_{A_2}I_{B_2}}\,\frac{\nu_{A_2}\nu_{B_2}}{\nu_{AB}^2}\cdot\frac{g_{0AB}^2}{g_{0A_2}g_{0B_2}}\,e^{\frac{2U'}{kT}}\,{}^{*} \qquad (3.34)$$

For instance, for reaction of oxidation of nitrogen, with good accuracy:

$$\frac{p_{NO}^2}{p_{N_2}p_{O_2}}=K_p'(T)=\frac{64}{3}e^{-\frac{43000}{RT}},$$

where R = 2 cal/mole•degree.

Here it is approximately considered that masses, frequencies and moments of inertia of all three molecules are identical; $U' = -21.4$ kilocalories/mole, ratio of statistical weights is equal to 16/3 (see § 2).

If gas constitutes a mixture in which there occurs a whole

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*The factor 4 appeared from ratio of symmetry factors $\sigma_{A_2}\sigma_{B_2}/\sigma_{AB}^2$; $\sigma_{AB} = 1$ $\sigma_{A_2} = \sigma_{B_2} = 2$; see footnote on p. 240. Just during dissociation, here it is assumed that

$$Z_{\text{кол}}=\frac{kT}{h\nu},\quad Z_{\text{эл}}=g_0.$$

series of reactions, then for each of reactions it is possible in an analogous way to derive a law of mass action connecting similarly to formula (3.32), the numbers of particles participating in the reaction and their statistical sums. Substitution of expressions for statistical sums gives equilibrium constants. Numbers of particles participating in many reactions are related with each other by conditions of conservation of number of atoms of every type, similar to (3.29).

The set of laws of mass action for each of reactions and conditions of conservation of number of atoms will form a system of nonlinear algebraic equations, which determine chemical composition, i.e., numbers of different particles N_i in dependence upon temperature and density of gas (or pressure) and initial atomic composition of mixture. As was shown by one of the authors [6], this system has a unique solution; i.e., equilibrium chemical composition of mixture is determined uniquely. By forming expression for energy of type (3.31), we can calculate internal energy of mixture. On the basis of general formula for free energy $F(T, V, N_i)$ and thermodynamic formulas (3.9), (3.10), it is also possible to obtain expression for energy and pressure, and with help of formula (3.8) — an expression for entropy of mixture.

As an example of such calculations can serve calculation of composition and thermodynamic functions of air, taking into account dissociation of molecules of N_2, O_2 and reactions of oxidation of nitrogen [3, 5]. Other reactions, leading to formation of NO_2, O_3, etc., practically do not affect calculations, since concentrations of these components turn out to be extraordinarily small.

Chemical composition and thermodynamic functions of air are illustrated in Tables 3.1 and 3.2.

§ 5. Ionization and Electronic Excitation

Just as dissociation of molecules, ionization of atoms (and molecules) begins at values of kT considerably smaller than ionization potential I. Cause of this is the same as in the case of dissociation: statistical weight of free state of electron is very great.

Potentials of first ionization of majority of atoms and molecules change from 7 to 15 ev ($I/k \sim 80{,}000 - 170{,}000^{\circ}K$).* The exception is mainly atoms of alkali metals with very low ionization potentials. Ionization begins usually at temperatures on the order of several or ten thousand degrees earlier, the lower the ionization potential and the more rarefied the gas.

With increase of temperature, degree of ionization increases, and when temperature becomes on the order of several tens of thousands of degrees, practically all atoms turn out to be singly ionized. In hydrogen, process of ionization is thus finished; upon further heating, the gas remains completely ionized and consists of protons and electrons; every particle accomplishes only translational motion, and heat capacity is equal to $\frac{3}{2}k$ per particle.

In gas of heavier atoms, after first ionization there starts the second, then the third, etc. Usually the following ionization begins still before complete termination of the preceding one, so that at temperatures higher than several tens of thousands of degrees,

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*For instance $I_O = 13.6$ ev, $I_N = 14.6$ ev, $I_{O_2} = 12.1$ ev, $I_{N_2} = 15.6$ ev, $I_{NO} = 9.3$ ev.

in the gas there are present ions with several charges, but if gas consists of mixture of several elements, then there are present ions with several charges of every element.

Just as during dissociation of molecules, internal energy of ionized gas is composed of energy of thermal motion of particles (atoms, ions, electrons) and potential energy, which is equal to expenditures in breaking away of electrons from atoms and ions. Furthermore, in region of ionization, a certain role can be played by energy of electronic excitation of atoms and ions.

Let us consider for simplicity a gas consisting of atoms of one element, and assume, as this most frequently occurs, that all molecules, if gas is not monatomic, in region of noticeable ionization are completely dissociated into atoms. Let us assume that 1 g of gas contains N atoms. Let us designate by I_m potentials of consecutive ionizations: I_1 is energy, necessary for breakaway of first electron from neutral atom, I_2 is energy for breakaway of electron from singly ionized atom, etc. In order to detach from the atom m electrons, it is necessary to expend the energy

$$Q_m = I_1 + I_2 + \ldots + I_m \quad (I_0 = 0). \tag{3.35}$$

Let us assume that at given temperature T and density ρ or specific volume V, in 1 g of gas there are N_0 neutral atoms, N_1 singly ionized atoms, etc. For brevity we will call ion with charge equal to m an m-ion; number of m-ions in 1 g we designate by N_m (neutral atoms are a particular case of m-ions). Number of free electrons will be designated by N_e. Assuming that gas is sufficiently rarefied and electrons obey statistics of Boltzmann,*

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*Degenerate electron gas will be considered in § 12.

we have to ascribe to every particle of gas a thermal energy of translational motion 3/2 kT. Furthermore, m-ion possesses energy of electron excitation W_m.

If we measure internal energy from non-ionized state of gas at zero temperature, then specific internal energy per initial atom can be written in the form*

$$\varepsilon = \frac{3}{2} N(1+\alpha_e)kT + N\sum_m Q_m\alpha_m + N\sum_{m} W_m\alpha_m, \tag{3.36}$$

where α_e is degree of ionization of gas, i.e., number of free electrons per initial atom ($\alpha_e = N_e/N$); $\alpha_m = N_m/N$ are concentrations of m-ions. Concentrations α_m are related with each other by conditions of conservation of number of atoms

$$\sum N_m = N, \quad \sum \alpha_m = 1 \tag{3.37}$$

and conservation of number of charges

$$\sum mN_m = N_e, \quad \sum m\alpha_m = \alpha_e. \tag{3.38}$$

Pressure of ionized gas**

$$p = N\rho(1+\alpha_e)kT. \tag{3.39}$$

Equilibrium concentrations of ions satisfy equations which are analogous to law of mass action for dissociation. This is understandable since process of ionization can be treated as the chemical reaction of "dissociation" of an atom or ion; for instance, process of breakaway of the m + 1-st electron from an m-ion can be written in symbolic form:

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*If gas at low temperatures is polyatomic to ε it is necessary to add energy of dissociation.

**Let us note that, just as for dissociation, formulas (3.36) for energy and (3.39) for pressure are accurate also in the case of non-equilibrium ionization, if by T we understand "translational" temperature of particles.

$$A_m \rightleftarrows A_{m+1} + e, \quad m = 0,\ 1,\ 2,\ \ldots \tag{3.40}$$

"Law of mass action" for this reaction is easy to derive from general expression for free energy, just as this is done for reaction of dissociation. Let us write free energy of 1 g of ionized gas

$$F = -\sum_m N_m kT \ln \frac{Z_m e}{N_m} - N_e kT \ln \frac{Z_e e}{N_e}, \tag{3.41}$$

where Z_m and Z_e are statistical sums of m-ion and electron.

In thermodynamic equilibrium for constants T and V, free energy is minimum with respect to numbers of particles. By forming the variation δF with respect to change of number of m-ions due to their ionization by the scheme (3.40), considering then that $\delta N_m = -\delta N_{m+1} = -\delta N_e$, and numbers of all other particles do not change, and equating variation δF to zero, we will obtain

$$\frac{N_{m+1} N_e}{N_m} = \frac{Z_{m+1} Z_e}{Z_m}. \tag{3.42}$$

Translational sums of both ions cancel out, since masses of ions practically do not differ from each other. In the electronic part of statistical sum of ion (atom), we will separate the factor corresponding to zero-point energy (ground state):

$$Z_{\text{эл}} = \sum e^{-\frac{\varepsilon_k}{kT}} = e^{-\frac{\varepsilon_0}{kT}} \sum e^{-\frac{\varepsilon_k - \varepsilon_0}{kT}} = e^{-\frac{\varepsilon_0}{kT}} u.$$

After designating difference between energies $\varepsilon_k - \varepsilon_0$, which is simply excitation energy of ion in k-th state, by w_k, we will write transformed electronic sum u in the form

$$u = \sum_k e^{-\frac{w_k}{kT}} = g_0 + g_1 e^{-\frac{w_1}{kT}} + g_2 e^{-\frac{w_2}{kT}} + \ldots, \tag{3.43}$$

where g_0, g_1. . . are statistical weights 0.1 . . . of energy levels of ion; if the latter are not degenerate, g = 1.

Statistical sum of free electron consists of product of translational sum and statistical weight of free electron, which is equal to two, in accordance with two possible spin orientations. By noticing that difference between zero-point energies of m + 1-st and m-th ions is equal to ionization potential of m-ion $\varepsilon_{0\,m+1} - \varepsilon_{0\,m} = I_{m+1}$, and also dividing expression (3.42) by volume ($n_i = N_i/V$), we will obtain

$$\frac{n_{m+1}n_e}{n_m} = 2\frac{u_{m+1}}{u_m}\left(\frac{2\pi m_e kT}{h^2}\right)^{\frac{3}{2}} e^{-\frac{I_{m+1}}{kT}} = K_{m+1}(T) \qquad (3.44)$$

(m_e is mass of electron).

This formula is known by the name of Saha formula. By multiplying it by kT, we can obtain relationship for partial pressures $p_i = n_i kT$. For numerical calculations, Saha formula can be conveniently rewritten in the form of an equation relating concentrations of particles $\alpha_i = N_i/N = n_iV/N = n_i/N\rho$,

$$\frac{\alpha_{m+1}\alpha_e}{\alpha_m} = \frac{1}{\rho N} K_{m+1}(T), \quad m = 0, 1, 2 \ldots \qquad (3.45)$$

Equations (3.45), (3.37), (3.38) form a closed system of nonlinear algebraic equations for determination of concentrations of ions and electrons in dependence upon temperature and density of gas.

Usually there exists a certain range of temperatures in the region from 8000° to 30,000°K in which only the first ionization is important, and the second still does not start (potential of second ionization is approximately twice the potential of the first). In this range, equations are simplified, since of all the equations (3.45) there remains only one with m = 0. By noticing that in region of first ionization $\alpha_1 = \alpha_e = 1 - \alpha_0$ and omitting indices for α_1 and ionization potential, we will obtain formula for degree of ionization $\alpha = \alpha_1 = \alpha_e$:

$$\frac{\alpha^2}{1-\alpha} = 2\,\frac{u_1}{u_0}\,\frac{1}{\varrho N}\left(\frac{2\pi m_e kT}{h^2}\right)^{\frac{3}{2}} e^{-\frac{I}{kT}}, \qquad (3.46)$$

which is very similar to formula for degree of dissociation (3.26).

For $I/kT \gg 1$, $\alpha \ll 1$, degree of ionization is proportional to $\alpha \sim \rho^{-1/2} e^{-I/2kT}$, i.e., very rapidly increases with increase of temperature and slowly increases with decrease of density of gas. For gas of atoms of hydrogen, formula (3.46) is always accurate.

Energies of excited levels of atoms and ions usually are quite high, and are comparable with ionization potential. In a number of cases there are low lying levels (and they, of course, have to be considered during calculation), but their number is very limited. More detail about calculation of transformed electronic sums u will be given in the following section. Here we note that, as a rule, it is sufficient to consider only the first several terms in these sums, where in most cases the overwhelming role is played by first term, and sum simply reduces to statistical weight of ground state $u \approx g_0$. The fact is that in a not too dense gas, electron in atom or ion "prefers" to detach rather than to occupy a high energy level. In region of single ionization $T \sim 10{,}000^\circ$ to $20{,}000^\circ$K, quantity I_1/kT usually is on the order of 5-10. If we go to higher temperature, then I_1/kT will become a small quantity, and simultaneously singly ionized atoms disappear, since second ionization starts, and for the most wide-spread ions quantity I_{m+1}/kT all the same will be on the order of 5-10. Inasmuch as energies of excited levels in atoms have the same order as ionization potential, then even the second term in sum u will be, let us say, on the order of e^{-5}, i.e., very small. Due to this, it turns out that in electronic sums u, for the most wide-spread ions, the main role is played by the first term g_0.

During exact calculations, usually there are taken into account the first 5 to 10 levels in ions and atoms, where energies and statistical weights of them are taken from corresponding tables [7]. There are also tables of potentials of consecutive ionizations of different atoms [8].

Internal energy of gas can be calculated by the formula (3.36), which follows from the general expression for free energy (3.41) in accordance with thermodynamic formula (3.9). Energy of electronic excitation W thus is equal to (index of charge of ion m is omitted):

$$W = \frac{\sum w_k e^{-\frac{w_k}{kT}}}{\sum e^{-\frac{w_k}{kT}}} = -kT^2 \frac{\partial \ln u}{\partial T}. \tag{3.47}$$

Entropy according to (3.8) is obtained by means of differentiation of free energy with respect to temperature:

$$S = \sum_m N_m k \ln \frac{e^{\frac{5}{2}} V}{N_m} \left(\frac{2\pi M k T}{h^2}\right)^{\frac{3}{2}} u_m + \sum_m N_m \frac{W_m}{T} + \\ + N_e k \ln \frac{e^{\frac{5}{2}} V}{N_e} \left(\frac{2\pi m_e k T}{h^2}\right)^{\frac{3}{2}} 2. \tag{3.48}$$

If excitation can be disregarded, second term vanishes and $u_m = g_{0_m}$.

Most simple are calculations in the region of first ionization, where degree of ionization can be calculated simply by the formula (3.46). The starting ionization gives a considerable contribution to heat capacity and energy of gas, and consideration of it is absolutely necessary during calculation of thermodynamic functions.

The wide range of temperatures and densities in which atoms are multiply ionized was encompassed in work of V. V. Selivanov and I. Ya. Shlyapintokh [4]. Authors calculated ionization composition,* thermodynamic functions and shock adiabat of air at temperatures from 20,000 to 500,000°K and densities from 10 ρ_0 to 10^{-3} ρ_0 (ρ_0 is normal air density). How ionization composition and degree of ionization changes with change of temperature, and also how ionization influences thermodynamic functions can be seen from Tables 3.2 and 3.3 for air, which are based on calculations of V. V. Selivanov and I. Ya. Shlyapintokh.**

At very high temperatures*** (or very low densities), energy and pressure of thermal radiation may turn out to be comparable to energy and pressure of the substance. Under conditions when radiation is in thermodynamic equilibrium with substance (whether this condition is satisfied or not it must be specially checked in every specific case; see Chap. II), energy and pressure of radiation should be simply added to energy and pressure of gas.

"Specific" energy of equilibrium radiation is equal to density of energy of radiation divided by density of substance:

$$\varepsilon_\nu = \frac{U_\nu}{\rho} = \frac{4\sigma T^4}{c\rho}, \tag{3.49}$$

and pressure of radiation

$$p_\nu = \frac{U_\nu}{3} = \frac{4\sigma T^4}{c}. \tag{3.50}$$

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*Generalization of the above-written equations to the case when gas is a mixture of elements is not difficult.

**In Table 3.2, data [4] pertain only to temperatures of 20,000°K and above.

***For air of normal density, these are temperatures above a million degrees.

Table 3.3. Composition of Ionized Air of Normal Density $\rho_0 = 1.29 \cdot 10^{-3}$ g/cm^3 at High Temperatures*

T°, K	Атом	0	1^+	2^+	3^+	4^+	5^+	6^+	e
20 000	N	0,589	0,201						0,48
	O	0,172	0,036						
50 000	N	0,018	0,451	0,321	0,001				1,35
	O	0,0065	0,303	0,048					
100 000	N		0,012	0,275	0,463	0,04			2,65
	O		0,005	0,09	0,113	0,005			
250 000	N				0,005	0,183	0,603		2,65
	O				0,005	0,020	0,114	0,074	
500 000	N					0,017	0,75	0,025	5,2
	O						0,010	0,200	

---

*Concentrations are defined as ratios of numbers of particles of given type to number of initial atoms.
0 are neutral atoms, 1^+ are singly ionized, etc.
e are electrons; N and O are ions of nitrogen and oxygen.

Entropy of radiation can be found with help of general thermodynamic relationships:

$$S_\nu = -\frac{\partial F_\nu}{\partial T}, \quad F_\nu = -T\int \frac{\varepsilon_\nu}{T^2}\,dT = -\frac{4\sigma T^4}{3c\varrho}, \quad S_\nu = \frac{16\sigma T^3}{3c\varrho}. \qquad (3.51)$$

In work [4], thermodynamic functions of air were calculated, taking into account equilibrium radiation.

§ 6. Electronic Statistical Sum and Role of Excitation Energy of Atoms

An isolated atom (ion, molecule) located in an infinite space possesses infinite number of energy levels, which converge to continuum, which corresponds to states with detached electron (ionized states). Formally electron statistical sum u contains infinite number of terms and diverges. Average excitation energy of atom W, calculated by formula (3.47) with infinite number of terms, is equal to ionization potential, since excitation energies of higher states asymptotically approach ionization potential.

This difficulty, which appears during purely formal calculation of u and W, has only an apparent character. In fact the atom never is isolated, but is located in a gas of finite density. Dimensions of electronic orbit rapidly increase during transition to higher states of electron in atom and finally become comparable with average distance between particles of gas, which is equal approximately to $r \approx N^{-1/3}$ (here by N we designate number of particles in 1 cm^3). Trajectories of electrons moving along such large orbits are distorted due to the presence of neighboring particles, and an electron which is removed from atomic core to a distance comparable with average distance between particles of gas essentially does not differ from a free electron. Thus, finiteness of density of gas imposes a limitation on number of possible states of atom and number of terms in electronic statistical sum, and also limits average excitation energy of atom.

Let us consider gas consisting of atoms of hydrogen. Results of consideration of hydrogen atoms have large generality, since highly excited states of any complicated atomic systems are very similar to excited states of an atom of hydrogen. If electron in complicated atom (ion, molecule) moves along a very great orbit, then field in which it is located is very close to Coulomb field of point charge (atomic core), and therefore structure of highly excited states of any atoms and ions is close to that of hydrogen. In order that we may extend results of consideration to multiply charged ions, we will into all formulas introduce charge of "nucleus," i.e., consider not hydrogen in the literal sense, but hydrogen-like atoms which are systems of positive "nucleus" with charge Z and an electron.

Levels of energy of hydrogen-like atom are characterized by principal quantum number n (see scheme of levels in Fig. 2.2 in § 2 of Chap. II). Energy of n-th level, measured from boundary of continuous spectrum, is equal, as is known, to $\varepsilon_n = -I_H Z^2/n^2$, where $I_H = 13.5$ ev is ionization potential of hydrogen. Absolute value of it $E_n = |\varepsilon_n| = I_H Z^2/n^2$ is binding energy of electron located on n-th level. Binding energy of ground state n = 1* is equal to ionization potential:

$$E_1 = I_H Z^2 = I.$$

Excitation energy of n-th state is equal to $w_n = \varepsilon_n - \varepsilon_1 = E_1 - E_n = I_H Z^2\left(1 - \frac{1}{n^2}\right)$. Transformed electronic statistical sum of hydrogen-like atom has the form

$$u = \sum g_n e^{-\frac{w_n}{kT}} = \sum 2n^2 e^{-\frac{I_H Z^2}{kT}\left(1 - \frac{1}{n^2}\right)},$$

where $g_n = 2n^2$ is statistical weight of n-th level.

Binding energy of electron on n-th level is equal to its Coulomb energy in field of nucleus at distance on the order of dimensions of orbit, namely, $E_n = Ze^2/2a$, where a is semi-major axis of elliptic orbit; $a = Ze^2/2E_n = e^2 n^2/Z I_H^2 = a_0 n^2/Z$, where

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*In distinction from the preceding, here we will assign to ground state index "1," and not "0," in accordance with equality to unity of principal quantum number n.

$a_0 = 0.53 \cdot 10^{-8}$ cm is Bohr radius. Statistical sum u in any case should be broken off at that value of n^* at which semiaxis of orbit becomes comparable with average distance between particles of gas, i.e., at $a = a_0 n^{*2}/Z = r$, $n^* = (Zr/a_0)^{1/2} \sim N^{-1/6}$ (n^* is less, the denser the gas). As a numerical example we will consider molecular hydrogen, which at room temperature was under atmospheric pressure and then was heated by a strong shock wave to temperature on the order of tens of thousands of degrees. Compression in shock wave is equal approximately to 10, so that under conditions of complete dissociation of molecules, number of atoms in 1 cm^3 will be $N \approx 5 \cdot 10^{20}/cm^3$. Average distance between atoms $r \approx N^{-1/3} = 1.3 \cdot 10^{-7}$ cm and limiting value $n^* = 5 (Z = 1)$. At a temperature of $T = 11{,}600°K = 1$ ev, statistical sum containing five terms is equal to $u = 2.00053$, i.e., is practically not different from statistical weight of ground state $g_1 = 2$. Average excitation energy of atom calculated by formula (3.47), taking into account five terms in the sum, is equal to $W = 0.003$ ev. At shown values of N and T, degree of ionization of hydrogen is $\alpha = 3 \cdot 10^{-3}$, i.e., ionizing energy, per atom $I_H \alpha = 0.04$ ev. Excitation energy W is small as compared to ionizing energy ($W/I_H \alpha = 0.075$). At higher temperature $T = 23{,}200°K \approx 2$ ev and the same density, $u = 2.212$ (also a little larger $g_1 = 2$), $W = 1.16$ ev. Degree of ionization now $\alpha = 0.22$; ionization energy from calculation for one initial atom is equal to $I_H \alpha = 3$ ev, and excitation energy, also for one initial atom, $W(1 - \alpha) = 0.9$ ev.

In this case excitation energy plays a noticeable role, but still it is less than ionizing energy. It is necessary to note that cut-off of upper levels in gas of finite density simultaneously lowers ionization potential exactly by a magnitude equal to value of binding energy of electron on boundary of cut-off, i.e., by the amount $\Delta I = E_{n*} = Ze^2/2r = ZI_H a_0/r = Z\ 7 \cdot 10^{-7} N^{-1/3}$ ev (N in $1/cm^3$).

In our example this decrease is equal to $\Delta I = 0.55$ ev, so that calculated degrees of ionization are somewhat too low.

At very high temperatures, ~50,000°K and above, excitation energy of remaining atoms of hydrogen becomes great, comparable with ionization potential, but then degree of ionization thus strongly increases and actual number of neutral atoms becomes small, so that contribution of excitation energy to energy of gas all the same is less than contribution of ionizing energy. This corresponds to the situation where it is more "favorable" for the electron to be completely detached from the atom than to occupy a high excited level.*

The earlier given estimate of number of terms in electronic sum most likely overstates the actual number of levels. Cut-off

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*This situation can be explained by means of the following semiqualitative reasoning, which is especially graphic in the limiting case of a gas of very low density. Ratio of probabilities of free and bound states of electron is proportional to ratio of translational and electronic statistical sums ($Z_{trans} \sim V \sim 1/\rho$). Electronic sum in the limit of low densities, when in it there participates a very large number of terms, can roughly be represented as follows:

$$Z_{\text{эл}} = \sum g_n e^{-\frac{\varepsilon_n}{kT}} = \sum 2n^2 e^{\frac{I_H}{n^2kT}} \sim \int_0^{n^*} n^2\,dn \sim n^{*3}.$$

But $n^* \sim r^{1/2}$, so that $Z_{el} \sim V^{1/2} \sim \rho^{-1/2}$. Hence $Z_{trans}/Z_{el} \sim \sim V^{1/2} \sim \rho^{-1/2}$. Thus, with decrease of density in the limit of low densities, in spite of increase of number of possible bound states, probability of breakaway of electron from atom all the same increases faster.

of higher levels in atoms and ions is considerably affected by the direct influence of electrostatic field of the nearest neighboring charge particle — the Stark-effect.

Furthermore, in a sufficiently rarefied gas, binding energy of electron moving along limiting orbit with dimension $a \sim r$, $E_{n*} = \Delta I = 7 \cdot 10^{-7} N^{-1/3}$ ev turns out to be less than kT (in our example $\Delta I = 0.55$ ev, and temperatures were 1 and 2 ev). Kinetic energy of electron in hydrogen-like atom is equal to its binding energy at given level. It is doubtful whether it has special meaning to consider a bound electron which binding energy and kinetic energy are less than kT. Practically every "collision" with free electron will knock a weakly bound electron from the atom. Certain authors therefore break off the electronic sums still more sharply, at that level where binding energy of electron is equal to kT.

To problems connected with lowering of ionization potentials in ionized gas and problem of calculation of electronic statistical sums there is dedicated a whole series of works [9-13, 34]. It is necessary to say that here there does not exist a single common opinion, and various authors offer different schemes for breaking off of electronic sums. Luckily, calculations show that variation in number of terms considered in electronic sums, as a rule, little affects thermodynamic functions of gases. But lowering of ionization potentials as a result of cut-off of upper levels sometimes noticeably affects ionization composition of gas (see work [14]).

In conclusion of this paragraph, let us note that phenomenon of cut-off of upper excited levels in atoms, ions, and molecules has experimental confirmation. In spectra of low-pressure arc discharges usually there is not observed more than 5-10 spectral lines of Balmer hydrogen series, which is connected with transitions of electron from upper excited level to ground level. Even in spectra of gaseous nebulae, density of which is extremely low (order of tens of particles per 1 cm^3), there is not observed more than 50-60 Balmer lines.

§ 7. Approximate Method of Calculation in Region of Multiple Ionization

Calculations of ionization equilibrium, which are the basis for finding of thermodynamic functions of gas at high temperatures, require very great and labor-consuming calculating work. For every pair of values of temperature and density, it is necessary to solve a nonlinear system of algebraic equations for determination of concentrations of ions of various charges, which is still more complicated if gas contains atoms of several elements. Essentially, within a wide range of temperatures and densities, tables are composed only for air. Certainly, at the contemporary level of computer technology, the problem of large numerical calculations to a considerable degree loses its severity, but still for practical purposes it is useful to have a simple method of approximation which would make it possible rapidly and with minimum expenditure of labor to calculate degree of ionization and thermodynamic functions of any gas within a wide range of temperatures and densities in the region of high temperatures, when atoms are multiply ionized. In this section there will be described such a method, which was proposed by one of the authors [15], which in its extreme simplicity possesses accuracy which is fully sufficient for solution of majority of practical problems.

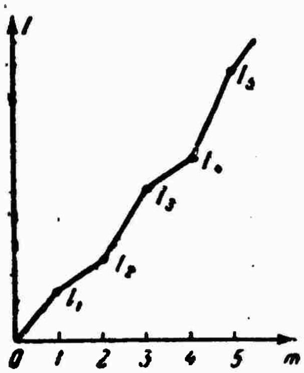

Fig. 3.1. Transition to continuous curve I(m).

We consider a gas, consisting of atoms of one element.

At the basis of method of approximation there are made two basic assumptions. We will, first of all, consider numbers of ions in 1 cm^3 n_m and potentials of ionization I_{m+1} as continuous functions of charge of ion m, while connecting discrete values of n_m and I_{m+1} by continuous curves. Function I(m) is constructed by means of connection of points I_m on diagram of I, m (Fig. 3.1) by a continuous curve, let us say, by means of connection of neighboring points by straight line segments. System of recursion formulas of Saha (3.44) thus can be transformed into a differential equation in the function n(m), if we introduce differentiation in place of finite differences:

$$n(m+1)=n(m)+\frac{dn}{dm}, \quad \Delta m=1.$$

Ratio of electronic statistical sums of ions u_{m+1}/u_m usually changes in a very irregular way during transitions from one charge m to another for a given element or transition to other elements; however, this ratio always has the order of unity. Let us assume it to be approximately equal to one. After this the system of Saha formulas can be written in the form of a differential equation:

$$\left(1+\frac{d\ln n}{dm}\right)n_e=AT^{\frac{3}{2}}e^{-\frac{I(m+1)}{kT}}, \qquad (3.52)$$

$$A=2\left(\frac{2\pi m_e k}{h^2}\right)=4{,}8\cdot10^{15}\ \text{см}^{-3}\cdot\text{deg}^{-3/2}=6\cdot10^{21}\ \text{см}^{-3}\cdot\text{ev}^{-3/2}.$$

Simultaneously conditions of conservation of numbers of particles and numbers of charges (3.37), (3.38) will be written in integral form:

$$\int n(m)\,dm = n, \tag{3.53}$$

$$\int mn(m)\,dm = n_e. \tag{3.54}$$

Consideration of results of exact calculations, just as consideration of system of Saha equations conducted below, shows that in gas there are always present in considerable number ions of two, and a maximum of three charges. Consequently, distribution function n(m) has the form of a very narrow and sharp peak near a certain value m_{max}, which, of course, depends on temperature and density of gas.

From this follows the second assumption. Let us assume, approximately, that average value of charge of ions, which coincides with average number of free electrons per initial atom

$$\bar{m} = \frac{\int mn(m)\,dm}{\int n(m)\,dm} = \frac{n_e}{n}, \tag{3.55}$$

is exactly equal to the value m_{max}, at which distribution function of ions n(m) passes through maximum. It is obvious that this assumption is all the more accurately, the sharper and narrower the peak of distribution n(m) is.

Designating by $\bar{I}$ ionization potential of ions with "average" charge $\bar{m}$ and noticing that at point of maximum of peak, derivative dn/dm = 0, we will obtain from (3.52) with help of (3.55) the following expression, which relates $\bar{m}$ and $\bar{I}$:

$$\bar{m} = \frac{AT^{\frac{3}{2}}}{n} e^{-\frac{I}{kT}}. \tag{3.56}$$

In order to transform this expression into an equation for finding of average charge (or degree of ionization) in dependence upon temperature T and density (number n of initial atoms in 1 cm^3), it is necessary to determine relation between $\bar{I}$ and $\bar{m}$. Here there is a certain arbitrariness connected with the purely symbolic question in exact theory about assigning of indices to ionization potentials.

If we designate ionization potential of m-ion by I_{m+1} (ionization potential of neutral atom I_1), then formally we should set $\bar{I} = I(\bar{m} + 1)$. Sometimes ionization potential of m-ion is designated by I_m (ionization potential of neutral atom I_0). In this case, in Saha formula (3.44) instead of I_{m+1}, it is necessary to write I_m, and formally it would be necessary to set $\bar{I} = I(\bar{m})$.

Certainly, if we consider heavy elements and very high temperatures, when degree of ionization is so high that $\bar{m}$ has the order of several tens, such arbitrariness numerically does not lead to essential variation in number $\bar{m}$ (since then $I_{m+1} - I_m \ll I_m$).

However, in region of small ionization, when average charge of ions is on the order of several units, such arbitrariness noticeably affects results of calculations of $\bar{m}$ and thermodynamic functions, which is connected with the approximate character of replacement of discrete quantities by continuous functions.

Comparison of results of approximate and exact calculations shows that best agreement is obtained if, as before, we designate ionization potential of m-ion by $I_{m+1} = I(m + 1)$, considering that $I_0 = I(0) = 0$, but refer "average" value of potential $\bar{I}$ to point $m + \frac{1}{2}$, i.e., consider $\bar{I} = I(\bar{m} + \frac{1}{2})$. This is quite natural, if we consider that in reality the series of discrete values of m is divided by finite intervals $\Delta m = 1$.

By taking the logarithm of (3.56), we will obtain simple transcendental equation for determination of $\bar{m}(T, n)$:

$$I\left(\bar{m}+\frac{1}{2}\right)=kT\ln\frac{AT^{\frac{3}{2}}}{\bar{m}n}. \qquad (3.57)$$

Thanks to logarithmic dependence of right side on $\bar{m}$, it is sufficient to make two to three successive approximation in order to find very exactly the root $\bar{m}$ with help of graph of function I(m).

Let us be convinced of the fact that distribution of ions over charges always has character of a narrow peak, and find the law of decrease of sides of the peak of distribution function n(m).

By combining consecutively the written Saha formulas for various m = 0, 1, 2 . . . , setting in them preliminarily the ratio of electronic statistical sums equal to one, and using definition of "average" potential (3.56), we will obtain:

$$\frac{n_{m+l}}{n_m}=\exp\left[-\sum_{i=1}^{l}\frac{I_{m+i}-\bar{I}}{kT}\right],$$

$$\frac{n_{m-l}}{n_m}=\exp\left[-\sum_{i=0}^{l}\frac{\bar{I}-I_{m-i}}{kT}\right],$$

where l = 1, 2, 3 . . .

Let us select m equal to that value at which n_m is maximum. $\bar{I}$ approximately corresponds to ionization potential of such ions, so that all terms in sums are positive, and concentrations of ions decrease on both sides of the maximum. In order to estimate law of decrease and width of peak, we will cross over in these formulas to continuous functions n(m), I(m). Expanding approximately

$$I(m)\approx\bar{I}+\left(\frac{dI}{dm}\right)(m-\bar{m}),$$

we will obtain Gaussian distribution curve

$$n(m)=n_{\max}\exp\left[-\left(\frac{m-\bar{m}}{\Delta}\right)^2\right] \qquad (3.58)$$

with half-width of peak

$$\Delta=\sqrt{\frac{2kT}{(dI/dm)}}. \qquad (3.59)$$

If we consider that on the average for various elements and various ionizations ionization potentials increase with charge of ion faster than the charge itself, i.e., that $dI/dm > I/m$, we will find that

$$\Delta < \sqrt{\frac{2kT\bar{m}}{\bar{I}}} = \sqrt{\frac{2\bar{m}}{\bar{x}_1}}, \quad \bar{x}_1 = \frac{\bar{I}}{kT}. \tag{3.60}$$

After substituting in this formula numerical values of $\bar{x}_1$ and $\bar{m}$, which are found, for instance, with help of Table 3.3 for air, we will see that $\Delta < 1$, i.e., that peak indeed is narrow.*

Approximate formulas for thermodynamic functions are obtained from exact formulas if, in accordance with the above made approximations, we consider that distribution of ions $n(m)$ constitutes a very narrow peak — almost a δ-function near the value of $\bar{m}$, i.e., if we consider that all ions in gas possess one non-integer "average" charge $\bar{m}$. Specific internal energy (3.36) thus takes the form

$$\varepsilon = \frac{3}{2} N (1 + \bar{m}) kT + NQ(\bar{m}) \tag{3.61}$$

(energy of electronic excitation will be disregarded). Here continuous function $Q(m)$ analogously to $I(m)$ is constructed graphically by means of connection by a continuous curve of discrete values of Q_m determined by formula (3.35). Let us note that best coincidence with exact calculations is obtained if in formula (3.61) we set $\bar{Q} = Q(\bar{m})$, in distinction from $\bar{I} = I(\bar{m} + \frac{1}{2})$. Pressure is equal to

$$p = n(1 + \bar{m}) kT. \tag{3.62}$$

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*The fact that the peak of distribution n_m is narrow, on the order of the "finite" difference $\Delta m = 1$ itself, in general deprives the transition to differentiation with respect to m of meaning. However, actually the method has turned out to be better than its foundation.

Specific entropy (3.48) (if we disregard electronic excitation and assume statistical weight of all ions to be identical and equal to g) is obtained equal to

$$S = Nk \ln \left(\frac{2\pi MkT}{h^2}\right)^{\frac{3}{2}} \frac{e^{\frac{5}{2}} g}{n} + Nk\bar{m} \ln \left(\frac{2\pi m_e kT}{h^2}\right)^{\frac{3}{2}} \frac{e^{\frac{5}{2}} g}{n \cdot \bar{m}}. \qquad (3.63)$$

By considering S = const and using formula (3.57), we will obtain equation of adiabat in parametric form:

$$\frac{T^{\frac{3}{2}}}{n} \exp\left\{\bar{m}\left[\frac{I\left(\bar{m}+\frac{1}{2}\right)}{kT} + \frac{5}{2}\right]\right\} = \text{const.} \qquad (3.64)$$

As the parameter serves $\bar{m}$; const in the right side is determined by values of T_0, n_0, through which the adiabat passes.

The above method of calculation of degree of ionization and thermodynamic functions is easily generalized to the case of a mixture of gases. For instance, in mixture of two elements, average charges of ions of each of the elements $\bar{m}_1$, $\bar{m}_2$ are found from system of two transcendental equations,

$$I_1\left(\bar{m}_1 + \frac{1}{2}\right) = I_2\left(\bar{m}_2 + \frac{1}{2}\right) = kT \ln \frac{AT^{\frac{3}{2}}}{n(c_1\bar{m}_1 + c_2\bar{m}_2)}, \qquad (3.65)$$

where c_1, c_2 are atomic concentrations of both elements, I_1, I_2 are curves of their ionization potentials, and n is total number of initial atoms in 1 cm^3. Specific internal energy is equal to

$$\varepsilon = \frac{3}{2} N(1 + c_1\bar{m}_1 + c_2\bar{m}_2)kT + Nc_1Q_1(\bar{m}_1) + Nc_2Q_2(\bar{m}) \qquad (3.66)$$

etc. In many cases, however, it does not have much meaning to complicate calculations thus. If potentials of consecutive ionizations of atoms of various elements do not strongly differ from each other, it is expedient to introduce "average" curve of potentials I(m), while considering all atoms as identical and averaging values of consecutive potentials over all elements in accordance with their percentage content in the mixture.

Table 3.4. Comparison of Approximate Calculations of Degree of Ionization and Internal Energy of Air with Exact Calculations*

$T°, K$	$1+\bar{m}$	$\varepsilon, \frac{eV}{атом}$	$1+\bar{m}$	$\varepsilon, \frac{eV}{атом}$
	$\rho_0=1,29\cdot10^{-3}$ g/cm^3		$\rho=10^{-2}\rho_0$	
30 000	1,68 1,77	16,6 23	2,30 2,21	33 33
50 000	2,4 2,42	40,5 47,8	3,35 3,26	83 80
100 000	3,72 3,75	126 140	5,10 5,16	243 252

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*Upper figures in each pair are obtained by method of approximation [15]; lower figures are taken from work of V. V. Selivanov and I. Ya. Shlyapintokh [4].

In Table 3.4 there are compared results of approximate calculations of degree of ionization and internal energy of air with exact data of V. V. Selivanov and I. Ya. Shlyapintokh [4]. It is clear that even for small degrees of ionization, where error should be especially great, method of approximation does not give bad accuracy. At high degrees of ionization, error does not exceed several percent.

The method truely transmits irregularities of change of $\bar{m}$ and ε with temperature and density, which correspond to sharp jumps in ionization potentials which appear during transitions from ions with filled electron shells to ions with unfilled shells. Calculations have shown that the method also gives good accuracy for xenon. Inasmuch as curves of ionization potentials for all elements are similar to one another, it is possible to rely on the fact that the approximate method will provide sufficient accuracy also in the case of any other gas.

§ 8. Interpolation Formulas and Effective Adiabatic Index

A direct result of calculations of thermodynamic functions is tables composed in the form of a grid of temperatures and densities (or temperatures and pressures). Use of tables during solution of gas-dynamic problems is connected with large inconveniences. It is much more pleasant to deal with simple interpolation formulas, which more or less accurately approximate the tabular data. Exceptional interest is presented by such an approximation of real functions, with which adiabatic index determining behavior of hydrodynamic process approximately turns out to be constant. Introduction of constant effective adiabatic index permits using self-similar and exact solutions of equations of gas dynamics, which, as a rule, it is possible to obtain only for a gas with constant heat capacity.

Adiabatic relations between some two thermodynamic parameters, for instance T and ρ or p and ρ, during consideration of incomplete excitation of vibrations, dissociation, and ionization no longer are described by equations of type of Poisson adiabats. It is possible formally to determine at every point the index γ in such a way that in neighborhood of this point true adiabat approximately coincides with equation of Poisson adiabat. For this it is obviously necessary to set:

$$\left(\frac{\partial \ln T}{\partial \ln \varrho}\right)_s = \gamma' - 1 \quad \text{or} \quad \left(\frac{\partial \ln p}{\partial \ln \varrho}\right)_s = \gamma''.$$

However, then indices corresponding to different pairs of thermodynamic parameters differ from each other. Therefore, with introduction of effective adiabatic index γ in the interesting range of T and ρ or p and ρ, it is necessary to define it so that it best corresponds to nature of gas-dynamic process.

Third equation of gas dynamics in general is the equation of conservation of energy, and in order to close the system of equations in hydrodynamics of an ideal fluid,* it is sufficient to introduce relation between specific internal energy and pressure and density $\varepsilon(p, \rho)$. Usually this relation is described by the formula

$$\varepsilon=\frac{1}{\gamma-1}\frac{p}{\rho}.$$

Therefore, for determination of effective adiabatic index in the interesting range of p and ρ we should compose a table for the combination

$$\gamma-1=\frac{p}{\rho\varepsilon} \tag{3.67}$$

and select a certain constant value of $\gamma - 1$, which best approximates actually non-identical values of this combination. As a result, equation of adiabat $d\varepsilon + p\,dV = 0$ $(V = 1/\rho)$ will take the form of Poisson adiabat $p \sim \rho^{\gamma}$, $\varepsilon \sim \rho^{\gamma-1}$ with effective constant value of γ.

Specific internal energy in dependence upon temperature and density is the most conveniently approximated by formula of the power type

$$\varepsilon=aT^{\alpha}V^{\beta} \tag{3.68}$$

with constant a, α and β.

In region of excitation of oscillations, heat capacity does not depend on density and $\beta = 0$. In the region of dissociation and

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*In hydrodynamics of an ideal fluid there are not considered viscosity and thermal conduction.

and ionization, heat capacity always increases with decrease of density of gas, since there is then increased degree of dissociation or ionization, and corresponding expenditures of energy increase. Therefore index β is always positive. Index α is always greater than 1, since heat capacity increases with increase of temperature in region of incomplete excitation of vibrations, as well as in regions of dissociation and ionization.

During approximation of function $\varepsilon(T, V)$ by formula (3.68) with constant indices α and β and approximation of function $p(\varepsilon, \rho)$ or $p(\varepsilon, V)$ by equation (3.67) with constant index γ, the three constants α, β and γ cannot be chosen independently.

Functions $p(\varepsilon, V)$ and $\varepsilon(T, V)$ have to satisfy the general thermodynamic relationship:

$$p+\left(\frac{\partial \varepsilon}{\partial V}\right)_T=T\left(\frac{\partial p}{\partial T}\right)_V.$$

It is easy to verify by means of direct substitution that three indices α, β, γ are related to each other by the condition

$$\gamma-1=\frac{\beta}{\alpha-1}, \qquad (3.69)$$

which holds, of course, only in the case when they are considered to be constant. During the described interpolation, which is easy to check with help of equation of adiabat $d\varepsilon + p\,dV = 0$, adiabatic relations of T and ρ and ε and ρ also are characterized by a single adiabatic index γ, just as in the case of the Poisson adiabat:

$$T\sim\varrho^{\gamma-1};\quad \varepsilon\sim\varrho^{\gamma-1};\quad p\sim\varrho^{\gamma}\quad \gamma=\text{const}.$$

This is obtained in spite of the dependence of heat capacity on temperature and volume.

For illustration of the numerical values of adiabatic index, in Table 3.2 there is presented the combination $1 + p/\rho\varepsilon = \gamma$ in region of multiple ionization of air. We see that index γ decreases with decrease of density.

In ranges of temperatures 10,000°-250,000°K and densities $10\rho_0$-$10^{-3}\rho_0$ (ρ_0 is normal density), internal energy of air in rough approximation can be described by interpolation formula (3.68) with following values of constants:

$$\varepsilon = 8{,}3\left(\frac{T^\circ}{10^4}\right)^{1{,}5}\left(\frac{\varrho_0}{\varrho}\right)^{0{,}12} \text{ ev/mole} . \qquad (3.70)$$

By formula (3.69) effective adiabatic index is equal to $\gamma = 1.24$.

It is important that index γ, determined by formula (3.67), is changed much less than indices α and β in formula (3.68). This situation is extremely favorable, since for analysis of adiabatic processes the relation $\varepsilon(T, V)$ actually is not needed; it is sufficient to have relation $\varepsilon(p, V)$ or $p(\varepsilon, V)$, which is given by equation (3.67).

It is necessary to note that effective adiabatic index and exponents α and β in interpolation formula (3.68) quite weakly change during transition from one gas to another if we try to approximate a wide range of temperatures and densities. This is understandable, since curves of ionization potentials in general are always similar to one another; they differ in details, which influence behavior of energy and pressure in small regions of variation of temperature and density of gas.

§ 9. Shock Adiabat Under Conditions of Dissociation and Ionization

Parameters of shock front in gas with constant heat capacity were calculated in Chapter I. In case of a strong wave, when pressure behind the front is much higher than initial $p_1 \gg p_0$, compression in front tends to limiting value $h = (\gamma + 1)/(\gamma - 1)$.

Thus, in a monatomic gas (inert gases, vapors of metals) $c_V = \frac{3}{2}Nk$, $\gamma = 5/3$ and $h = 4$; in a diatomic gas with non-excited vibrations $c_V = 5/2NkT$, $\gamma = 7/5$ and $h = 6$.* Already from the formula for h in case of gas with constant heat capacity, we may see that compression in front is greater, the larger the heat capacity is and the nearer the adiabatic index is to unity. The tendency to increased compression during increase of heat capacity is retained in the general case, when heat capacity depends on temperature and density. If diatomic gas is so dense that vibrations are excited still before beginning of dissociation, then during transition to stronger shock waves heat capacity behind the front increases, tending to the value $c_V = \frac{7}{2}NkT$, adiabatic index tends to $\gamma = \frac{9}{7}$, and compression behind the front is increased to $h = 8$.

Dissociation and ionization lead to further increase of compression. It is important to note that magnitude of compression is affected only by that part of heat capacity which is connected with potential and internal energy of particles: energy of dissociation and ionization, rotational and vibrational energy of molecules, energy of electronic excitation of atoms and ions. Increase of specific heat capacity due to increase of number of particles in gas does not affect compression, since simultaneously with increase of energy of translational motion of particles, pressure of gas increases. Change of number of particles is not directly reflected on adiabatic index γ, which is determined by

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*Maximum compression in practice, which is equal to 6, is attained in a diatomic gas with non-excited vibrations only at very low initial temperatures T_0. Otherwise, at those temperatures behind the front at which vibrations are still not excited, pressure ratio p_1/p_0 is not large enough for shock wave to be "strong."

compression. This is easy to verify if we represent internal energy in the form of the sum $\varepsilon = \varepsilon_{\text{trans}} + Q$, where in Q there is included potential energy and energy of internal degrees of freedom of particles. Noticing that pressure $p = \frac{2}{3}\rho\varepsilon_{\text{trans}}$, we will substitute these expressions in formula for shock adiabat (1.71). By disregarding initial energy and pressure, i.e., considering shock wave to be strong, we will obtain after elementary calculation that magnitude of limiting compression is equal to

$$h = 4 + \frac{3Q}{\varepsilon_{\text{пост}}}\,{}^{*)}. \qquad (3.71)$$

This quantity differs from 4, which corresponds to a monatomic gas more, the greater the relative role of potential and internal energy is.

In region of dissociation and ionization, potential energy usually turns out to be higher than translational energy of particles, and compression in the front is great, on the order of 10-12; especially great is compression for small initial density, when degrees of dissociation and ionization are very high at given temperature.**

Compression in region of ionization for heavy gases does not remain constant during increase of amplitude of wave. Relative contribution of potential energy after passage of maximum of compression, in period of dissociation or first ionization, gradually

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*In article of authors [16] instead of formula (3.71) there was given incorrect relationship $h = 4/(1 - 3Q/\varepsilon_{\text{trans}})$ (formula (2.5)).

**Thus, for instance, when through air with initial pressure $p_0 = 10^{-4}$ atm there are propagated shock waves with velocities $D \sim 6.5 - 12$ km/sec (Mach number $M \sim 20 - 35$), compression behind front is equal approximately to 17.

decreases, since translational energy increases faster than potential energy due to increase of number of particles. Thus compression also gradually decreases. It occurs in this way until all electrons are detached from some shell of the atoms. Between ionization potentials of the last of the electrons of this shell and the first of the electrons of the following closed shell, there always is a great gap. This gap is especially great between L- and K-shells. Thus, for instance, in nitrogen this is 97 ev and 550 ev, in oxygen 137 ev and 735 ev. Therefore, in air there exists quite a wide interval of amplitudes of waves, approximately in range of temperatures from 500,000° to 700,000°K, when all electrons in atoms of oxygen and nitrogen filling L-shells have already been detached, and ionization from K-shells still has not begun: in gas there are present only helium-like ions. When during further increase of amplitude of wave there starts breaking away of K-electrons, expenditures of energy on ionization again sharply increase, relative contribution of potential energy, just as in beginning of first ionization, is increased, and compression passes through a second, clearly pronounced maximum.

Pressure behind strong shock wave front, as follows from equations of conservation of momentum and mass (1.61), (1.62), is little sensitive to magnitude of compression, especially during large compressions, and is approximately proportionally to square of velocity of propagation of wave D:

$$p_1 = \varrho_0 D^2 \left(1 - \frac{1}{h}\right) \qquad (3.72)$$

(for instance, at h ~ 10 with accuracy up to ~10%).

With still greater accuracy, on the order of 1%, specific enthalpy behind front is proportional to square of velocity:

$$w_1 = \frac{D^2}{2}\left(1 - \frac{1}{h^2}\right) \tag{3.73}$$

[this expression follows from formulas (1.61), (1.62), (1.64)].

Temperature, which in gas with constant heat capacity is also proportional to square of velocity, under conditions of dissociation and ionization increases with increase of amplitude of wave much more slowly.

In region of first ionization, this occurs due to relative increase of expenditures of energy on ionization, i.e., of the quantity $Q/\varepsilon_{\text{trans}} \sim Q/T$; subsequently, when fraction of potential energy in internal energy decreases as compared to translational energy, delayed temperature rise is explained by increase of number of particles, to which $\varepsilon_{\text{trans}}$ and p are proportional:

$$\varepsilon_{\text{пост}} = \frac{3}{2} N (1 + m) kT, \quad p = n (1 + \overline{m}) kT.$$

Let us note that after occurrence of total ionization, when with increase of amplitude of shock wave and temperature behind the front $\varepsilon_{\text{trans}}$ increases and Q remains constant, compression during increase of amplitude tends to 4 (if we do not consider thermal radiation). This one may see from formula (3.71). For instance, in hydrogen, in region of total dissociation and ionization potential energy per atom is equal to 15.74 ev (energy of dissociation of H_2 is 2.24 ev per atom; ionizing energy is 13.5 ev), translational energy per atom (energy of proton and electron) is equal to 3 kT = 3 T ev, i.e.,

$$h = 4 + \frac{15{,}74}{T_{\text{эв}}} \to 4 \text{ when } T \to \infty$$

(total ionization in hydrogen, at atomospheric density before the wave, occurs at T ~ 100,000°K ~ 10 ev).

For illustration of the presented considerations about influence of dissociation and ionization on parameters behind shock front, we present Table 3.5, which contains results of calculation of these parameters for air for normal initial density. Data for low temperatures in region of excitation of vibrations are taken from book of Ya. B. Zel'dovich [17]; calculations in region of dissociation and beginning of first ionization were made by Davis [18]. Within a wide range of temperatures from 20,000° to 500,000°K, parameters of front were calculated by V. V. Selivanov and I. Ya. Shlyapintokh in work [4], already cited above.

Table 3.5. Parameters Behind Wave Front in Air for Normal Conditions Before the Front
$p_0 = 1$ atm, $T_0 = 293°K$

$T°$, K	D, km/sec	p_1, atm	ρ_1/ρ_0	$T°$, K	D, km/sec	p_1, atm	ρ_1/ρ_0
293	0,33	1	1	14 000	9,31	1000	11,10
482	0,70	5	2,84	20 000	11,8	1650	10,10
705	0,98	10	3,88	30 000	15,9	2980	9,75
2260	2,15	50	6,04	50 000	23,3	6360	8,97
4000	3,35	127	8,58	100 000	40,1	19 200	8,62
6000	4,54	236	9,75	250 000	81,6	76 500	7,80
8000	5,64	366	10.30	500 000	114,0	143 900	6,27
10 000	6,97	561	11,00				

Calculations of parameters behind shock wave front in air in wide range of initial pressures from normal to $p_0 \sim 10^{-5}$ atm were made by I. B. Rozhdestvenskiy [19] and H. F. Gorban' [20] (for temperatures behind the front not exceeding 12,000°K).

In a number of works there were calculated parameters of shock wave front in other gases: in argon and hydrogen (N. A. Prokof'yev

[21]), in argon (Resler and others [22]), in xenon (Sabol [23]), in hydrogen and xenon (S. R. Kholev [24]). Phenomena in all gases do not differ from each other qualitatively and shock adiabats are very similar to each other.

Calculated adiabats in argon and xenon agree well with experimental adiabats obtained on the basis of study of shock waves in shock tubes. Regarding air — here there is satisfactory agreement of calculations with experiment. It is necessary to note that behavior of shock adiabat in region of dissociation strongly depends on which of the two previously questionable values is ascribed to dissociation energy of nitrogen: 7.38 ev or 9.74 ev. Experiments of Christian and others [25] studying shock waves in air with help of shock tube confirmed that experimental shock adiabat is nearer to calculated adiabat corresponding to dissociation energy of nitrogen of 9.74 ev. In favor of this value witness experiments of Model, [26], who measured velocity of front and (by an optical method) temperature behind the front.

§ 10. Shock Adiabat Taking into Account Equilibrium Radiation

At very high temperatures (or very low densities of gas), when energy and pressure of equilibrium radiation are comparable with energy and pressure of substance, radiation should be considered during calculation of shock adiabat (of course, preliminarily, we should check to see if equilibrium of radiation with substance under specific conditions of the problem is established.

Let us consider a very strong shock wave propagating through a cold gas, and assume that fluxes of radiation in both sides of the front are equal to zero. Let us assume also that behind the shock wave front radiation is equilibrium (without being interested here in the question of the process of establishment of equilibrium). Thus, we consider problem from a purely thermodynamic point of view, as this usually is done during derivation of shock adiabat.* Let us stress that we consider the non-relativistic case, when velocities of shock wave and substance are much less than velocity of light, and energies of substance and radiation are much less than rest energy of substance. Let us introduce into equations of conservation of fluxes of momentum and energy on shock wave front the energy and pressure of radiation behind the front $\varepsilon_{\nu 1}$, $p_{\nu 1}$ (see § 13, Chap. I and § 17, Chap II). Laws of conservation on front will be written in the form

$$\left.\begin{aligned} \rho_1 u_1 &= \rho_0 D, \\ p_1 + p_{\nu 1} + \rho_1 u_1^2 &= \rho_0 D^2, \\ \varepsilon_1 + \varepsilon_{\nu 1} + \frac{p_1}{\rho_1} + \frac{p_{\nu 1}}{\rho_1} + \frac{u_1^2}{2} &= \frac{D^2}{2}. \end{aligned}\right\} \tag{3.74}$$

In order to simplify problem for the purpose of clarification of role of radiation, we will consider that gas possesses constant heat capacity and adiabatic index γ and obeys usual equation of state:

$$p = A\rho T, \quad A = \text{const}; \quad \varepsilon = \frac{1}{\gamma - 1} AT = \frac{1}{\gamma - 1} \frac{p}{\rho}.$$

By substituting in (3.74) $\varepsilon_{\nu 1}$ and $p_{\nu 1}$ according to formulas (3.49), (3.50), expressing pressure p_1 and energy ε_1 in terms of temperature T_1, and eliminating u_1 with help of the first of equations (3.74), we will obtain relationships corresponding to formulas (3.72), (3.73), in which radiation is not considered:

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*This problem was considered by Sachs [27].

$$\left.\begin{aligned} A\varrho_0 hT_1+\frac{4\sigma T_1^4}{3c}&=\varrho_0 D^2\left(1-\frac{1}{h}\right),\\ \frac{\gamma}{\gamma-1}A\varrho_0 hT_1+\frac{16\sigma T_1^4}{3c}&=\frac{\varrho_0 D^2}{2}h\left(1-\frac{1}{h^2}\right),\end{aligned}\right\} \qquad (3.75)$$

where $h = \rho_1/\rho_0$ is compression in front of shock wave. Let us further eliminate D from these equations and solve the obtained expression for T_1:

$$\frac{4\sigma T_1^3}{3Ac\varrho_0}=\frac{h(h-h_0)}{(7-h)}, \qquad (3.76)$$

where $h_0 = (\gamma + 1)/(\gamma - 1)$ is limiting compression in strong shock wave without taking into account radiation.

This relationship can be considered as an equation determining compression h in dependence upon amplitude of shock wave, which can be characterized by temperature behind the front T_1.

Quantity in left side of equation (3.76), which is proportional to T_1^3, is simply ratio of radiation pressure to pressure of substance behind shock wave front $p_{\nu 1}/p_1$. From formula (3.76) it follows that if radiation pressure is relatively small, $p_{\nu 1}/p_1 \ll 1$, then $h \approx h_0$, i.e., compression is equal to usual magnitude $h_0 = (\gamma + 1)/(\gamma - 1)$. In the limit of a very strong wave, when $p_{\nu 1}/p_1 \sim T_1^3 \to \infty$, compression h tends to $h_\infty = 7$. This result should have been expected, since equilibrium radiation from thermodynamic point of view behaves as ideal gas with adiabatic index $\gamma = 4/3$ (see § 3, Chap. II), which corresponds to limiting compression in shock wave equal to 7.

In interval between two limiting cases $\frac{p_{\nu 1}}{p_1} \to 0$ and $\frac{p_{\nu 1}}{p_1} \to \infty$, compression h with increase of amplitude of wave monotonically changes from $h_0 = (\gamma + 1)/(\gamma - 1)$ to $h_\infty = 7$, independently of whether

$h_0 > 7$ or $h_0 < 7$, i.e., independently of whether adiabatic index of gas, without taking into account radiation is less than or larger than 4/3.

In limiting case, when energy and radiation pressure are much larger than energy and pressure of substance, i.e., when second terms in left sides of equations (3.75) are much larger than the first, temperature behind the front $T_1 \sim D^{1/2}$, in distinction from usual case $T_1 \sim D^2$, without taking into account radiation (in gas with constant heat capacity).

We recall that relative role of energy and pressure of equilibrium radiation are greater, the less the density of the substance is: $p_\nu/p \sim 1/\rho$ (in gas with constant number of particles).

For instance, in completely ionized hydrogen, radiation pressure is equal to pressure of gas at $T = 10^6$ °K, if number of particles (protons and electrons) $n = 10^{19}$ $1/\text{cm}^3$; if, however, $n = 10^{16}$ $1/\text{cm}^3$, pressures are equal at $T = 10^5$ °K.

2. Gas of Particles with Coulomb Interaction

§ 11. Rarified Ionized Gas

We will consider deviations of ionized gas from idealnesses which are caused by Coulomb interaction of charged particles. We will be limited in this paragraph to the case of weak nonideality, when terms of Coulomb interaction in thermodynamic functions can be considered as small corrections to terms corresponding to an ideal gas.

In order that ionized gas may be considered as ideal, it is necessary that energy of Coulomb interaction of neighboring particles be small as compared to their energy of thermal motion, i.e., that there be satisfied the condition $(Ze)^2/r_0 \ll kT$, where Z is average charge of particles (ions, electrons), and $r_0 \approx n^{-1/3}$ is average distance between them; n is number of particles in 1 cm^3 of gas. This condition can be rewritten in the form

$$n \ll \left(\frac{kT}{Z^2e^2}\right)^3 = 2.2\cdot 10^{8}\left(\frac{T^\circ}{Z^2}\right)^3 \ 1/cm^3 \tag{3.77}$$

For instance, for degree of ionization on the order of unity ($Z \sim 1$) and $T \sim 30{,}000^\circ K$, for idealness it is necessary that $n \ll 6.2\cdot 10^{21}$ $1/cm^3$ (for comparison let us remember that number of molecules in air of normal density is equal to $2.67\cdot 10^{19}$ $1/cm^3$).

Coulomb corrections to thermodynamic functions for weak nonideality can be calculated using method of Debye and Hückel as this is done in book of L. D. Landau and E. M. Lifshits [1] (see also work of B. L. Timan [11]). Around each of ions or electrons there will be formed a nonuniformly charged cloud of neighboring particles, where distribution of density of charge in this cloud is determined by law of Boltzmann in accordance with electrostatic potential created by joint action of central charge and cloud. Solution of Poisson equation for distribution of electrostatic potential over radius r near central ion with charge Z_1e in first approximation leads to formula

$$\varphi_i = Z_ie\exp\frac{(-r/d)}{r},$$

where d is so-called Debye radius, which characterizes dimensions of cloud,

$$d = \left(\frac{4\pi e^2}{kT}\sum n_iZ_i^2\right)^{-\frac{1}{2}} = 6.90\left(\frac{T^\circ}{n\overline{Z^2}}\right)^{1/2} cm \tag{3.78}$$

(n_1 is number of ions with charge Z_1e in 1 cm^3, electrons also are included here in concept of "ions"; for them Z = -1).

Statistical consideration by method of Debye-Hückel is valid if in the cloud there are contained many particles, i.e., if Debye radius d is much larger than average distance between particles $r_0 \approx n^{-1/3}$. Condition $d \gg r_0$ leads to condition $n \ll \left(\frac{kT}{4\pi e^2 \overline{Z^2}}\right)^3 = 1.1 \cdot 10^5 \left(\frac{T^0}{\overline{Z^2}}\right)^3 \frac{1}{\text{cm}^3}$, which is still more rigid than condition of ideality of gas (3.77). Thus, Debye consideration assumes very weak nonideality of gas.

Near center at $r \ll d$ $\varphi_i = \frac{Z_i e}{r} - \frac{Z_i e}{d}$. First term is potential created by central ion itself, and second term $-\varphi_i' = -Z_i e/d$ is potential created by surrounding charges in the place where the given ion is located. Coulomb energy of gas in volume V, according to general electrostatic formula, is equal to

$$E_{\text{кул}} = V \cdot \frac{1}{2} \sum e Z_i n_i \varphi_i' = -V e^3 \sqrt{\frac{\pi}{kT}} \left(\sum n_i Z_i^2\right)^{\frac{3}{2}}. \tag{3.79}$$

Correction to free energy can be found by means of integration of thermodynamic relationship $E/T^2 = -\partial/\partial T(F/T)$:

$$F_{\text{кул}} = \frac{2}{3} E_{\text{кул}} = -\frac{2}{3} e^3 \sqrt{\frac{\pi}{kTV}} \left(\sum N_i Z_i^2\right)^{\frac{3}{2}}, \tag{3.80}$$

where $N_i = n_i V$ is total number of particles of i-th type in volume V. Correction to pressure:

$$p_{\text{кул}} = -\left(\frac{\partial F_{\text{кул}}}{\partial V}\right)_{T, N_i} = \frac{E_{\text{кул}}}{3V}. \tag{3.81}$$

On the average, between particles there act attractive forces, since every ion surrounds itself chiefly with charges of opposite sign. Therefore, Coulomb energy and pressure are negative.

Coulomb interaction influences state of gas in two ways. First, it decreases energy and pressure (and also entropy:

$S_{coul} = -\frac{\partial F_{coul}}{\partial T} = \frac{E_{coul}}{3T}$). Second, and this effect is the most important, it shifts ionization equilibrium in the direction of higher degree of ionization.

Really, free electron in interacting gas possesses negative potential energy, i.e., it is also as if somewhat bound with ions; therefore, for breakaway of electron from atom or ion, it is necessary now to expend somewhat less work, which corresponds to effective decrease of ionization potentials. Decrease of ionization potential is determined by change of not the total, but only the free Coulomb energy, since "turning on" of Coulomb forces of interaction changes entropy of system, whereas change of potential energy coincides with change of total energy only in reversible process.

In order to derive formula for ionization equilibrium, taking into account Coulomb interaction, we will proceed just as in § 5. Let us write total free energy of system in the form

$$F = F_{\text{ид}} + F_{\text{кул}},$$

where F_{id} is expressed by formula (3.41), and F_{coul} is expressed by (3.80), and form variation δF with respect to variation of number of m-ions as a result of their ionization.

Using the condition $\delta N_m = -\delta N_{m+1} = -\delta N_e$ and equating variation δF to zero, we will obtain in place of (3.42) the corrected expression for "law of mass action." In order not to confuse here statistical sum with charge, we will note statistical sums by a "tilde" ($\tilde{Z}$):

$$\frac{N_{m+1}N_e}{N_m} = \frac{\tilde{Z}_{m+1}\tilde{Z}_e}{\tilde{Z}_m} e^{\frac{\Delta I_{m+1}}{kT}}, \tag{3.82}$$

where quantity ΔI_{m+1}, which is equal to change of Coulomb parts of chemical potentials

$$\Delta I_{m+1} = \mu_{m,\text{кул}} - \mu_{m+1,\text{кул}} - \mu_{e,\text{кул}};\ \mu_{i,\text{кул}} = \left(\frac{\partial F_{\text{кул}}}{\partial N_i}\right)_{T,V},$$

can be treated as decrease of ionization potential of m-ions (we recall that $\tilde{Z}_{m+1}\tilde{Z}_e/\tilde{Z}_m \sim \exp(-I_{m+1}/kT)$).

Calculation gives for correction to ionization potential the quantity

$$\Delta I_{m+1} = 2(Z_m+1)e^3\sqrt{\frac{\pi}{kT}}\left(\sum n_i Z_i^2\right)^{\frac{1}{2}}, \tag{3.83}$$

where Z_m is charge of m-ion; essentially, $Z_m = m$.

If we take into account definition of Debye radius (3.78), (3.83) can be rewritten in the form

$$\Delta I_{m+1} = \frac{(Z_m+1)e^2}{d} = \frac{Z_{m+1}e^2}{d}. \tag{3.84}$$

Decrease of ionization potential of m-ion is exactly equal to energy of Coulomb interaction of m + 1-ion, which is obtained as a result of ionization of m-ion, with detached electron, if the latter is located at a distance equal to Debye radius.

In accordance with conditions of validity of method of Debye and Hückel and condition of weak nonideality, formula (3.84) is valid if $d \gg r_0$, i.e., $\Delta I \ll kT$.

In region of first ionization, formula (3.84) takes the form ($i = 0, 1, e$; $Z_0 = 0$, $Z_1 = 1$, $Z_e = -1$):

$$\Delta I_1 = 2e^3\left(\frac{2\pi n\alpha}{kT}\right)^{\frac{1}{2}}, \tag{3.85}$$

where $\alpha = n_e/n = n_1/n$ is degree of ionization.

In region of multiple ionization, by replacing, as we did in § 7, all ions by ions with the same "average" charge $\bar{m} = \frac{n_e}{n}$ (n – number of initial atoms in 1 cm^3) and considering $\bar{Z}_i^2 = \bar{m}^2$, we will obtain for change of "average" ionization potential:

$$\overline{\Delta I} = 2(\bar{m}+1)e^3\left[\frac{\pi\bar{m}(\bar{m}+1)n}{kT}\right]^{\frac{1}{2}}. \qquad (3.86)$$

As an example we will consider air at a temperature of T = = 100,000°K and normal density n = $5.34 \cdot 10^{19}$ 1/cm^3. Without taking into account Coulomb interaction, we have under these conditions degree of ionization $\bar{m}$ = 2.72 and "average" ionization potential $\bar{I}$ = 60 ev ($\bar{I}/kT$ = 6.9). Correction to "average" ionization potential with this value of $\bar{m}$ is equal to $\overline{\Delta I}$ = 5.4 ev ($\overline{\Delta I}/kT$ = = 0.63), i.e., Coulomb interaction decreases "average" ionization potential almost by 10%, which corresponds in the following approximation to increase of degree of ionization approximately by 14%.*

Influence of Coulomb corrections on shift of ionization equilibrium in argon at T = 45,000°K and $p \sim 10^{-3}$-10^2 atm is considered in work [14]. This influence turned out to be quite noticeable, while corrections to thermodynamic functions did not exceed 1%.

§ 12. Dense Gas. Elements of Fermi-Dirac Quantum Statistics for Electron Gas.

Above, in examining of ionized gas, it always was assumed that free electrons obey classical Boltzmann statistics. Strictly speaking, electron gas is described by Fermi-Dirac, quantum statistics which only in case of sufficiently high temperatures or sufficiently low densities becomes Boltzmann statistics. This

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*Formally, under the considered conditions, we are at the limit of applicability of this method, since $\overline{\Delta I}$ = 5.4 ev is only a little less than kT = 8.6 ev.

transformation occurs if temperature of electron gas is much higher than so-called degeneracy temperature T_0, which is determined by number of electrons in 1 cm^3 n:

$$T_0 = \frac{1}{8}\left(\frac{3}{\pi}\right)^{\frac{2}{3}} \frac{h^2}{m_e k} n^{\frac{2}{3}} = 4{,}35 \cdot 10^{-11} n^{\frac{2}{3}} \text{ deg.} \tag{3.87}$$

For usual gas densities and temperatures, at which due to ionization there appear free electrons, condition $T \gg T_0$ is much more than satisfied. For instance, for density of atmospheric air and approximately single ionization of atoms $n = 5.34 \times 10^{19}$ $1/cm^3$, degeneracy temperature $T_0 = 610^\circ K$, temperature of gas thus $T \sim 35{,}000^\circ K$, so that $T/T_0 \approx 60$. Condition of applicability of Boltzmann statistics can be unsatisfied either at very low temperatures, or at high densities of electron gas. First case, in consideration of gases, usually does not occur, since at low temperatures gases are not ionized.

Regarding, however, the second case, in a number of processes there will be formed a very dense, highly heated gas, in which there are present electrons. Usually such a situation occurs when an initially solid body is rapidly heated to very high temperatures, on the order of tens or hundreds of thousands of degrees,* and

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*For instance, during impacts of meteorites flying with high velocities on the order of several tens of km/sec against surface of a planet, during explosions of wires by an electrical current, during heating of anode needles in pulse X-ray tubes by electron impact (see work of V. A. Tsukerman and M. A. Manakova [28]), during heating of solid body by powerful shock wave, and others. We do not dwell here on such a classical object for application of quantum statistics as free electrons in metals under usual conditions.

essentially is turned into a dense gas, since at such temperatures energy of thermal motion frequently exceeds binding energy of atoms in solid or liquid substance.

For density on the order of density of solid body and, number of free electrons per atom on the order of unity, degeneracy temperature is equal to several tens of thousands of degrees (for instance, for $n = 5 \cdot 10^{22}$ $1/cm^3$ $T_0 = 59{,}000^\circ K$), i.e., even at a temperature of one hundred thousand degrees, it is in no way possible to describe electrons by Boltzmann statistics.

It is necessary to note that for densities on the order of density of solid body and temperatures of tens or hundreds of thousands of degrees, energy of Coulomb interaction of charged particles, electrons, and ions is comparable with their kinetic energy, and the electron — ion gas is essentially nonideal.*

Problem of determination of thermodynamic properties of gas under such conditions is approximately solved by method which constitutes a generalization of method of Thomas — Fermi for statistical description of atom in case of temperature different from zero. In order to expound the essence of this method it will be necessary for us to recall the basic ideas of Fermi-Dirac quantum statistics (for greater detail see, for instance [1]).

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*For instance, for $n = 5 \cdot 10^{22}$ and $Z = 1$, Coulomb energy $e^2/r \approx e^2 n^{1/3}$ is equal to kT at $T = 60{,}000^\circ K$. Kinetic energy of free electrons, which is determined not simply by temperature, but also by degeneracy temperature T_0, is also comparable to Coulomb energy, inasmuch as T_0 is thus equal to $59{,}000^\circ K$.

Let us consider a free* electron gas at zero temperature (so-called completely degenerate gas). Number of quantum states in element of volume dV and interval of absolute values of electron momenta from p to p + dp (number of cells in phase space of coordinates and momenta) is equal to $4\pi p^2 dp\, dV/h^3$. In each cell there can be found two electrons with oppositely directed spins, so that total number of quantum states in given interval dpdV is $8\pi p^2 dp\, dV/h^3$. According to the Pauli principle, in every quantum state, with given direction of spin, there can be not more than one electron.

N electrons located in volume V (n = N/V is number of electrons in 1 cm^3) fill all of the lowest energy states with momenta from 0 to p_0, so that

$$N = V\int_0^{p_0} \frac{8\pi p^2\,dp}{h^3} = \frac{8\pi p_0^3}{3h^3}V.$$

From this there follows the expression for maximum kinetic energy of electrons $\varepsilon_0 = p_0^2/2m_e$ – so-called (maximum) Fermi energy:

$$\varepsilon_0 = \frac{1}{8}\left(\frac{3}{\pi}\right)^{\frac{2}{3}}\frac{h^2}{m_e}\left(\frac{N}{V}\right)^{\frac{2}{3}} = \frac{1}{8}\left(\frac{3}{\pi}\right)^{\frac{2}{3}}\frac{h^2}{m_e}n^{\frac{2}{3}}. \tag{3.88}$$

Degeneracy temperature (3.87) is defined as $T_0 = \varepsilon_0/k$. Kinetic energy of N electrons in volume V is equal to:

$$E_k = V\int_0^{p_0} \frac{p^2}{2m_e}\frac{8\pi p^2\,dp}{h^3} = \frac{3}{5}\varepsilon_0 N \sim N^{\frac{5}{3}}V^{-\frac{2}{3}} \tag{3.89}$$

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*Free in the sense that forces do not act on electrons. At the same time it is assumed that electron gas does not spread out. Actually this can be imagined as an electrically neutral mixture of ions and electrons, in which average self-consistent field is considered to be equal to zero (everywhere, besides at boundaries of the body).

(Average kinetic energy of one electron is equal to $\frac{3}{5}\varepsilon_0$).

Inasmuch as electrons are assumed to be free, then kinetic energy at the same time is also equal to total energy $E_k = E$, and in virtue of thermodynamic relationship $TdS = dE + PdV$, referred to zero temperature, pressure of free degenerate electron gas is equal to

$$P = -\frac{dE}{dV} = \frac{2}{3}\frac{E_k}{V} = \frac{2}{5}\varepsilon_0 n = \frac{1}{20}\left(\frac{3}{\pi}\right)^{\frac{2}{3}}\frac{h^2}{m_e}n^{\frac{5}{3}}. \tag{3.90}$$

Pressure is proportional to density to the 5/3 power.

Relationship between pressure and kinetic energy $P = 2/3 \cdot E_k/V$ is the same as in a monatomic Boltzmann gas. This is understandable since "kinetic" pressure is determined by transfer of momentum by particles, and its relation to kinetic energy of particles is purely mechanical, not depending on type of statistics which the particles obey.

With increase of temperature, electrons which earlier filled the lowest energy levels pass into higher quantum states. In quantum statistics of Fermi-Dirac, it is proven that distribution function of particles over quantum states, i.e., average number of electrons in quantum state with energy ε, is

$$f = \frac{1}{e^{\frac{-\mu+\varepsilon}{kT}} + 1}, \tag{3.91}$$

where μ is a constant depending on temperature and density of electrons, an constituting the chemical potential of an electron gas. In free electron gas energy ε is equal to kinetic energy $\varepsilon = p^2/2m_e$. At zero temperature, distribution function is equal to 1 if $\varepsilon < \mu \left(\frac{-\mu + \varepsilon}{kT} = -\infty\right)$, and is equal to 0 if

$\varepsilon > \mu \left(\frac{-\mu + \varepsilon}{kT} = +\infty\right)$, i.e., we obtain the already found above distribution, where, as we may see from this reasoning, chemical potential of free gas coincides with Fermi energy ε_0. At temperature different from zero, distribution is "spread out," as shown in Fig. 3.2.

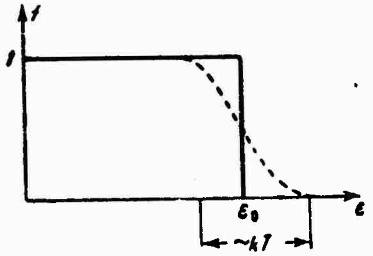

Fig. 3.2. Distribution function for electron gas according to Fermi — Dirac statistics.

Number of electrons in 1 cm with momenta in interval from p to p + dp is

$$\varrho(p)\,dp=\frac{8\pi p^2\,dp}{h^3}f=\frac{8\pi}{h^3}\frac{p^2\,dp}{e^{\frac{-\mu+\varepsilon}{kT}}+1}, \tag{3.92}$$

and total number of electrons per unit of volume is equal to

$$n=\int_0^{\infty}\varrho(p)\,dp=\frac{8\pi}{h^3}\int_0^{\infty}\frac{p^2\,dp}{e^{\frac{-\mu+\varepsilon}{kT}}+1}. \tag{3.93}$$

Thus formula determines in implicit form the chemical potential μ as a function of temperature and density.

Kinetic energy of electrons per unit of volume is equal to

$$\mathcal{E}_k=\int_0^{\infty}\frac{p^2}{2m_e}\varrho(p)\,dp=\frac{8\pi}{h^3}\int_0^{\infty}\frac{p^2}{2m_e}\frac{p^2\,dp}{e^{\frac{-\mu+\varepsilon}{kT}}+1}. \tag{3.94}$$

Statistics can be applied also to electron gas located in a potential field. It is clear that the field must change in space quite slowly, so that in elementary volume dV, throughout which the field can be considered to be constant, there are sufficiently many particles. Otherwise, application of statistics to particles loses its meaning.* If we designate electrostatic potential of field at

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*Field should change little at a distance on the order of wave length of electron.

point r by $\varphi(r)$, then energy of electron ε can be written in the form

$$\varepsilon = \frac{p^2}{2m_e} - e\varphi(r). \tag{3.95}$$

In statistical mechanics it is proven that if gas is located in a field, then in state of equilibrium its chemical potential μ must be identical at different points. Otherwise particles will flow from one place to another.

If we consider an electron gas located in a field at zero temperature, then, according to formulas (3.91), (3.95), distribution function f as before is equal to 1 if $\varepsilon = p^2/2m_e - e\varphi(r) < \mu$, and is equal to 0 if $\varepsilon = p^2/2m_e - e\varphi(r) > \mu$. Thus, maximum kinetic energy of electron at given point r is equal to $\varepsilon_0(r) = \mu + e\varphi(r)$. It now depends on coordinate, but maximum total energy of electron $p_0^2/2m_e - e\varphi(r) = \varepsilon_0 - e\varphi(r) = \mu$, which is equal to chemical potential, does not depend on the point (if it depended on coordinate, electrons would flow from place with higher to place with lower maximum energy).

Formulas (3.92) to (3.94) are also valid for a gas located in a field if by ε we understand quantity (3.95). Formula (3.93) now gives implicit relation of density of gas at point r, n(r) to quantity $\varepsilon_0(r) = \mu + e\varphi(r)$, i.e., to potential at given point and temperature T. At T = 0 this relation, as before, is expressed by formula (3.88).

§ 13. Thomas-Fermi Model of Atom and Strong Compression of a Cold Substance

During description of a dense gas according to method of Thomas-Fermi, there is not made a distinction between "free" and "bound" electrons, and gas is considered to consist not of ions and electrons, as at small densities, but of nuclei and electrons. Nuclei obey Boltzmann statistics and introduce their own contribution to total pressure and total specific thermal energy. At high temperatures this contribution corresponds to a usual monatomic gas:

$$P_a = n_a kT, \quad \varepsilon_a = \frac{3}{2}\frac{n_a}{\varrho} kT$$

(n_a is number of nuclei in 1 cm^3, ρ is density of substance). All of the energy of interaction of particles will be ascribed to electrons. For calculation of electronic parts of energy and pressure, gas is divided into atomic cells, each of which contains nucleus with charge Ze and Z electrons. For simplicity the cell is considered to be spherical. Volume of it V is taken equal to average volume in substance per nucleus: $V = 1/n_a$, and radius $r_0 = (3V/4\pi)^{1/3} = (3/4\pi n_a)^{1/3}$.

Between atomic cells in Thomas-Fermi model there do not act cohesive forces, so that this model does not describe bonds of atoms in a solid body. Cells exert on one another a positive pressure, which coincides with pressure of electron gas, i.e., model describes only repulsive forces and "thermal" pressure. Therefore, model gives reasonable results either for large densities, for a strongly compressed solid body, when repulsive forces sharply predominate over attractive forces of atoms, or at high temperatures, when cohesive forces can be disregarded. From what has been said, it follows that in the model of Thomas-Fermi, energies of "ionization," "excitation" and "thermal motion" of electrons no longer are calculated separately, as in examining of rarefied gases. They automatically are included in total electron energy of the atomic cell. In order to separate from it the "thermal" part of energy, which is specially related with existence of temperature, from total energy we should eliminate energy of cell of the very same volume, but corresponding to zero temperature. The same pertains also to pressure.

Let us first consider atomic cell at zero temperature, i.e., the statistical model of atom according to Thomas and Fermi.*
At the basis of this model lies the assumption that in complicated atoms with large number of electrons, majority of electrons possess high principal quantum numbers and their motion is quasiclassical.

Electrons in atom are considered as a gas located in a self-consistent electrostatic field quite slowly changing over radius** $\varphi(r)$, which is caused by charges of nucleus and electrons themselves. Thereby there is considered nonideality of the electron gas. To this gas there is applied Fermi-Dirac statistics.

Maximum kinetic energy of electron at given distance from nucleus r $\varepsilon_0(r) = \mu + e\varphi(r)$ is related with density of electrons at this point by formula (3.88), so that density is expressed in terms of potential by formula

$$n(r) = \frac{8\pi}{3} 2^{\frac{3}{2}} \frac{m_e^{\frac{3}{2}}}{h^3} [e\varphi(r) + \mu]^{\frac{3}{2}}. \tag{3.96}$$

Electrostatic potential $\varphi(r)$ satisfies Poisson equation:

$$\Delta\varphi = \frac{1}{r} \frac{d^2}{dr^2} [r\varphi(r)] = 4\pi e n(r), \tag{3.97}$$

which after substitution of (3.96) and introduction of new "potential"

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*To detailed account of this question is dedicated the book of Gambosh [29]. Short and clear account can be found in book of L. D. Landau and E. M. Lifshits [30].

**Possibilities of statistical description of electron gas in a field were discussed in the preceding section.

$\psi = \varphi + \mu/e$ (potential is determined with accuracy up to the additive constant) takes the form:

$$\frac{1}{r}\frac{d^2}{dr^2}(r\psi) = \frac{32\cdot 2^{\frac{2}{3}}\pi^2}{3}\frac{e^{\frac{5}{2}}m_e^{\frac{3}{2}}}{h^3}\psi^{\frac{3}{2}}. \tag{3.98}$$

To equation (3.98) there are attached boundary conditions. In the center, as $r \rightarrow 0$, field becomes Coulomb field of nucleus, i.e.,

$$\varphi(r) = \frac{Ze}{r} \text{ as } r \rightarrow 0. \tag{3.99}$$

Inasmuch as cell is electrically neutral, on the boundary its field is equal to zero (outside of the cell potential is constant):

$$\frac{d\varphi}{dr} = 0 \text{ for } r = r_0. \tag{3.100}$$

This condition is equivalent to the obvious relationship

$$Z = \int_0^{r_0} n(r)\, 4\pi r^2\, dr. \tag{3.101}$$

By introduction of dimensionless variables

$$x = \frac{r}{a},\ a = \frac{1}{4}\left(\frac{9\pi^2}{2}\right)^{\frac{1}{3}}\frac{a_0}{Z^{\frac{1}{3}}} = \frac{0{,}885a_0}{Z^{\frac{1}{3}}}, \tag{3.102}$$

where $a_0 = h^2/4\pi^2 m_e e^2 = 0.529\cdot 10^{-8}$ cm is Bohr radius and

$$\chi = \frac{r}{Ze}\left(\varphi + \frac{\mu}{e}\right) = \frac{r}{Ze}\psi. \tag{3.103}$$

equation (3.98) is reduced to universal form

$$x^{\frac{1}{2}}\frac{d^2\chi}{dx^2} = \chi^{\frac{3}{2}}. \tag{3.104}$$

Boundary conditions (3.99), (3.100) take the form:

$$\chi(0) = 1;\ \chi(x_0) = x_0\left(\frac{d\chi}{dx}\right)_{x_0}.$$

Dimensionless form of equations demonstrates character of similarity with respect to number of electrons Z. Namely, distribution of density over radius according to (3.96), (3.102), (3.103) can be written in the form

$$n(r) = Z^2 f\left(\frac{rZ^{\frac{1}{3}}}{b}\right), \quad b = 0,885a_0, \tag{3.105}$$

where function f is proportional to $(\chi/x)^{3/2}$.

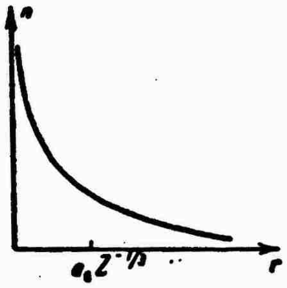

Fig. 3.3. Schematic distribution of electron density in free atom.

Solution of equation (3.104) with corresponding boundary conditions (this is done by means of numerical integration) gives distribution of potential and density of electrons over radius, after which it is possible to calculate all quantities which are interesting to us.

Electron density in free neutral atom which is not compressed by external forces, as the solution shows, extends to infinity: $\chi \to 0$, $n \to 0$ as $x \to \infty$* (Fig. 3.3). If as zero potential energy is taken the state in which all charges are separated to infinity, we should set potential φ equal to zero at infinity. Chemical potential thus becomes zero. Pressure on boundary of free atom which is not compressed by external forces, and consequently also pressure** in

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*Inasmuch as field of electrically neutral atom should decrease at infinity faster than r^{-2}, "potential" ψ decreases faster than r^{-1}; boundary condition in this case takes form $r\psi \sim \chi \to 0$ as $r \to \infty$.

**Pressure in system of interacting particles is composed of two parts: "kinetic," connected with motion of particles and their kinetic energy by usual relationship $P_k = 2n\varepsilon_k/3$, where n is number of particles in 1 cm^3, and ε_k is their mean kinetic energy; and "potential" energy, which is equivalent to forces acting on particles all of space are equal to zero. According to the virial theorem for an unfounded Coulomb field, total kinetic and potential energies of particles are connected by the relationship $2E_k^\infty = -E_p^\infty$. Total energy of atom $E^\infty = E_k^\infty + E_p^\infty = -E_k^\infty = \frac{1}{2}E_p^\infty$. Virial theorem in this case, in essence, expresses the fact that kinetic repulsion of electrons is exactly balanced by Coulomb attraction of them toward the nucleus, due to which total pressure, which is equal to sum of "kinetic" and "potential," at every point is equal to zero. Although electron density, in principle, extends to infinity, main charge is concentrated in a finite volume V_{ef}. According to (3.105), as the linear scale of this region serves Bohr radius a_0, where $V_{ef} \sim Z^{-1}$ (see Fig. 3.3). This follows also from virial theorem. Potential energy of atom in order of magnitude is equal to $E_p^\infty \sim -e^2Z^2/V_{ef}^{1/3}$. Kinetic energy according to (3.88), (3.89) is on the order of

$$E_k^\infty \sim \varepsilon_0 Z \sim \frac{h^2}{m_e} Z \left(\frac{Z}{V_{\text{эф}}}\right)^{\frac{2}{3}}.$$

From condition of mechanical equilibrium or virial theorem we will find $V_{ef} \sim (\frac{m_e e^2}{h^2})^3 Z^{-1} \sim a_0^3 Z^{-1}$. Total energy of atom is on the order of $E^\infty = E_p^\infty/2 \sim -e^2\, Z^{7/3}/a_0 \sim -I_H\, Z^{7/3}$. . Exact value of $E^\infty =$ $= -20.8Z^{7/3}$ ev; this is, in absolute value, the energy which it is necessary to expend in order to separate all charges of an atom

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[FOOTNOTE CONT'D FROM PRECEDING PAGE]

(in the given case Coulomb forces). Formally this separation follows from the relationship (at zero temperature) $P = -\partial E/\partial V =$ $= -\partial E_k/\partial V - \partial E_p/\partial V = P_k + P_p$. Kinetic pressure is always positive, potential pressure $P_p > 0$, if particles are repulsed, and $P_p < 0$, if they are attracted.

to infinity (energy of total ionization of atom).

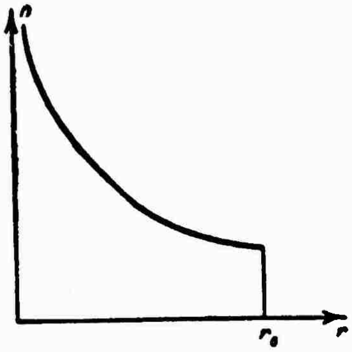

Fig. 3.4. Schematic distribtuion of electron density in "compressed" atom – in atomic cell of radius r_0.

Let us consider now a "compressed" atom, i.e., an atomic cell of finite volume V. Now pressure (equal to "external" force acting on 1 cm^2 of surface of cell is different from zero and positive. Consequently, also electron density on boundary of cell is finite (Fig. 3.4). Really, field on boundary of cell is lacking. Electrons at the boundary behave as free electrons and all of the pressure at the boundary is of "kinetic" orgin. "Kinetic" pressure, by definition, is equal to transfer of normal component of momentum to 1 cm^2 of surface of cell in 1 sec. Inasmuch as electrons are distributed over directions of motion isotropically,

$$P=\int_0^\infty \varrho(p,r_0)\,p\,\frac{v}{3}\,dp, \tag{3.106}$$

where $\rho(p, r_0)$ is distribution function over momenta at boundary of cell r_0, and $v = p/m_e$ is velocity of electrons. Pressure, as we should have expected, is equal to

$$P=\frac{2}{3}n(r_0)\,\varepsilon_k(r_0)=\frac{2}{5}n(r_0)\,\varepsilon_0(r_0), \tag{3.107}$$

where $\varepsilon_k(r_0) = \frac{3}{5}\varepsilon_0(r_0)$ is average kinetic energy of electrcn at boundary of cell. Pressures at all points are identical: $P = P_k + P_p$ = const, although "kinetic" and "potential" components change from point to point. "Kinetic" pressure P_k at any point is expressed in terms of kinetic energy by a formula of type (3.107).

By expressing total kinetic and potential energies of the entire cell E_k and E_p by integrals over volume of cell of energy densities, which are proportional to electron density, it is possible by means of direct calculation, to be convinced that*

$$PV = \frac{2}{3} E_k + \frac{1}{3} E_p. \tag{3.108}$$

Equation (3.108) can be derived from virial theorem applied to system of particles located in Coulomb field and occupying finite volume.** In particular, for a free atom P = 0 and $2E_k^{\infty} = -E_p^{\infty}$, as it was already said above.

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*During calculation of potential energy, it is necessary to break potential into two terms, which correspond to potential of nucleus and potential of electrons $\varphi = \varphi_a + \varphi_e$; $\varphi_a = Ze/r$:

$$E_p = E_{pe} + E_{pa} = -\frac{1}{2} 4\pi e \int_0^{r_0} r^2 dr\, n(r)\, \varphi_e(r) - 4\pi e \int_0^{r_0} r^2 dr\, n(r)\, \varphi_a(r) = \tag{3.109}$$
$$= -\frac{1}{2} 4\pi e \int_0^{r_0} r^2 dr\, n(r) \left[\varphi(r) + \frac{Ze}{r}\right]^0.$$

Factor 1/2 in E_{pe} is introduced because energy of interaction of every electron with every other one in the integral is taken into account twice. In order that potential energy be measured from the value corresponding to separation of all electrons to infinity, it is necessary to set potential on boundary of neutral cell $\varphi(r_0)$ equal to zero. Inasmuch as density on boundary of compressed atom is different from zero (it is proportional to pressure), chemical potential, in virtue of definition of $\varphi(r_0) = 0$, according to (3.96), is not equal to zero and is positive.

**Virial theorem for motion of system of particles in Coulomb field states: $2E_k = I = -\overline{\sum_i r_i F_i}$, where r_i is radius vector of i-th electron, and F_i is force acting on it. Averaging is carried out over all positions of electrons (or over time). By dividing

During compression of atom, pressure and density on boundary increase. Also energy of cell increases, in virtue of relationship $dE = -P\,dV$ $(P > 0)$. Physically this is obvious if we consider that the electron cloud which is not restrained by external forces while tending to reduce energy of system to a minimum spreads out to infinity. If we are interested in energy of compression of cell, then it is necessary to measure from energy of free atom, i.e., from total energy of cell $E(V)$ it is necessary to subtract energy of atom E^{∞}. Inasmuch as pressure in free atom is equal to zero, then from pressure it is not necessary to subtract anything.

Here we should stress that Thomas-Fermi model is essence describes only repulsive forces acting between atoms (atomic cells), which are equivalent to positive pressure, and does not describe attractive forces, which appear only during calculation of exchange energy. Therefore, the model cannot provide for binding of atoms in a solid body. In order to compress atomic cell to its dimensions in a solid body in Thomas-Fermi model, it is necessary to expend

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virial I into three components corresponding to forces acting on electron from other electrons I_{ee}, nucleus I_{ea}, and boundary I_0, and producing simple transformations (see [31]), we will obtain

$$I_0 = r_0 \overline{\sum_i |F_{\text{граница}}|} = 4\pi r_0^2 P = 3PV,$$

$$I_{ea} = \overline{\sum_i \frac{Ze^2}{r_i}} = -E_{pa},$$

$$I_{ee} = -e^2 \overline{\sum_i \sum_j \frac{r_i(r_i - r_j)}{|r_i - r_j|^3}} = -\frac{e^2}{2} \overline{\sum_i \sum_j \frac{1}{|r_i - r_j|}} = -E_{pe}.$$

By substituting all these terms into virial theorem, we will obtain (3.108).

work against forces of pressure, and energy of such a cell is larger than energy of free atom, whereas in reality pressure in solid body at zero temperature is equal to zero, and energy of bound state of atom is less than energy of free atom.

During small compressions of free atom in the considered model, when volume $V \gg V_{ef}$, electron density is redistributed only near boundary (Fig. 3.5), pressure and energy $\Delta E = E - E^{\infty}$ are small. Approximate dependence of pressure on volume of cell can be obtained by assuming that density on boundary r_0 is the same in first approximation as density at point $r = r_0$ in a free atom. As it is easy to verify, asymptotic solution of equation (3.104) for free atom as $x \to \infty$ has the form $\chi = 144\, x^{-3}$.

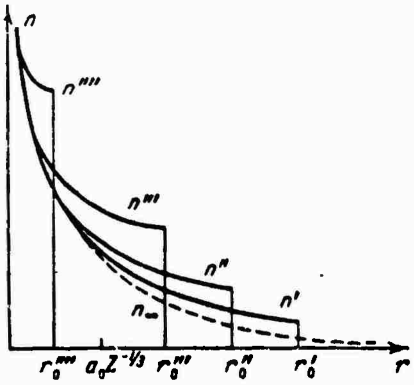

Fig. 3.5. Redistribution of electron density during compression of atom. n', n'', n''', n'''' are schematic distributions in cells of radii r_0', r_0'', r_0''', r_0''''. n_{∞} is distribution in free atom ($r_0 = \infty$).

According to (3.105) and (3.102), density on boundary

$$n(r_0) \sim Z^2 \left(\frac{\chi}{x}\right)^{\frac{3}{2}} \sim Z^2 x^{-6} \sim Z^2 r_0^{-6} Z^{-2} \sim r_0^{-6} \sim V^{-2},$$

and pressure according to formula (3.107) $P \sim n\varepsilon_0 \sim n^{5/3} \sim V^{-10/3}$ and does not depend on Z.

Considerable increase of pressure and energy starts during large compressions, when volume of atomic cell becomes on the order of and less than effective volume V_{ef}, which is occupied by the main part of the electrons in the atom. Electrons now occupy the whole volume of the cell (see Fig. 3.5), and average distance between particles $\bar{r}$ is on the order of $V^{1/3}$, and average density

$\bar{n} \sim Z/V$. Thus $E_k \sim Z\bar{n}^{2/3} \sim Z^{5/3}V^{-2/3}$, and $E_p \sim -Z^2/\bar{r} \sim Z^2V^{-1/3}$.

As can be seen from these relationships, during compression, kinetic energy increases faster than potential energy, and in the limit of small volumes, i.e., large densities of substance, $E_k \gg E_p$; $E \sim E_k$; $P \sim E_k/V$. All pressure becomes "kinetic" and limiting law has the form

$$p \sim Z^{\frac{5}{3}}V^{-\frac{5}{3}} \sim \bar{n}^{\frac{5}{3}}. \qquad (3.110)$$

Pressure of strongly compressed cold substance is proportional to density of substance ρ (to which average density of electrons $\bar{n}$ is proportional) to the 5/3 power, as for a free degenerate electron gas. Specific energy accordingly is proportional to $\varepsilon \sim \rho^{2/3}$.

It is necessary to say that actually these limiting laws become valid only at very high densities, which by about ten times exceed density of usual solid bodies. Actual dependences of pressure and energy of cold compression of solid bodies on density will be discussed in Chapter XI.

§ 14. Calculation of Thermodynamic Functions of Highly Heated Dense Gas by Thomas-Fermi Method

General scheme of thermodynamic description of a dense gas at high temperatures in the model of Thomas-Fermi was presented in beginning of preceding section. Generalization of equations of model of cold atomic cell to the case of temperature different from zero is made elementarily. At the basis lies the Poisson equation (3.97) for electrostatic potential in cell $\varphi(r)$,* which

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*Let us note that Poisson equation lies at basis of calculation of Coulomb interaction of given ion with electron-ion cloud forming around it in method of Debye-Hückel. However, in distinction from this method, here Coulomb energy is not assumed to be small as compared to kinetic energy, and for density of charges there is written an exact expression and, furthermore, for description of electrons there are used distribution functions not of Boltzmann, but of Fermi-Dirac.

as before satisfies boundary conditions (3.99) and (3.100), and also is assumed to be equal to zero on boundary of cell in order to provide an expedient reference for potential energy. However, instead of simple relationship (3.96) connecting electron density n(r) with potential, now there appears integral relationship (3.93) with distribution function f(p), which depends on temperature according to formula (3.91), where energy of electron is expressed, as before, by formula (3.95).

Just as before, the normalization condition (3.101) is valid. Total kinetic energy of cell is calculated by means of integration of density of kinetic energy (3.94) over volume of cell, but potential energy is expressed in terms of electron density and potential by formula (3.109).

For pressure formula (3.106) is accurate, if by $\rho(p, r_0)$ we now understand distribution function over momenta, which depends on temperature according to formula (3.92). As before we have the virial theorem, leading to relationship (3.108), which follows directly from expressions for P, E_k and E_p.

Certain difficulties are presented by calculation of entropy of cell S. Direct calculation of it with help of thermodynamic relationships and expressions for energy E and pressure P of cell was made by Brachman [32]. Less rigorously, by means of approximate calculation of statistical sum, Latter [31] found entropy. Entropy of cell is equal to

$$S=\frac{1}{T}\left[\frac{5}{3}E_k+2E_{pe}+E_{pa}-Z\mu\right], \tag{3.111}$$

where E_{pe} and E_{pa} are potential energies of interaction of electrons with each other and with nuclei (see formula (3.109)). For determination of chemical potential μ as function of T and V serves normalization condition (3.101).

It is possible to show that as $T \to 0$ the expression in parentheses tends to zero faster than T, so that $S \to 0$ in accordance with theorem of Nernst.

System of equations for determination of functions $\varphi(r)$ and $n(r)$, and also expressions for energy, pressure and entropy can be transformed to dimensionless variables (as scale of length there is introduced radius of cell r_0), where, as at zero temperature, model allows similarity transformation with respect to Z. At zero temperature distribution of density was expressed by formula (3.105), whence it follows that density on boundary of cell can be represented in the form $n(r_0) = Z^2 F(V \cdot Z)$ $(r_0 Z^{1/3} \to V \cdot Z)$; pressure, according to (3.107), in the form $P = Z^{10/3} F_1(V \cdot Z)$; and energy, according to (3.108), in the form $E = Z^{7/3} F_2(V \cdot Z)$.

At temperature different from zero these similarity relations are generalized in such a way that temperature always is contained in the form of combination $TZ^{-4/3}$, so that

$$PZ^{-\frac{10}{3}} = f(VZ, TZ^{-\frac{4}{3}}), \quad EZ^{-\frac{7}{3}} = f_1(VZ, TZ^{-\frac{4}{3}}).$$

Entropy and chemical potential always appear in the form of combinations SZ^{-1}, $\mu Z^{-4/3}$.

Equations of Thomas-Fermi model were solved numerically with help of electronic computer, and results of calculation of thermodynamic functions within a wide range of variables VZ and $TZ^{-4/3}$ (densities and temperatures) are given in the form of graphs in the article of Latter [31].*

From energy E there was subtracted energy of cold free atom E^{∞} (accordingly from E_k and E_p there were subtracted E_k^{∞} and E_p^{∞}).

Consideration of results of calculations shows that with increase of temperature in cell of given volume, kinetic and total energies and pressure monotonically increase.

Potential energy changes little — only due to redistribution of electron density, which with increase of temperature is equalized over the volume of the cell. In the limit of very high temperatures, when there is plotted degeneracy of an electron gas (for $kT \gg \frac{h^2}{m_e}(Z/V)^{2/3}$; see formula (3.87)), energy and pressure tend to their natural values:

$$E \approx E_k \approx \frac{3}{2} ZkT; \quad P \approx \frac{Z}{V} kT = \bar{n}kT.$$

If we isothermally compress atomic cell, pressure in it monotonically increases, and indeed, more slowly than in case of zero temperature, which may be seen at least from the fact that in the limit of high temperatures $P \sim 1/V$, whereas at $T = 0$ and $V \to 0$ $P \sim 1/V^{5/3}$. Energy at not too high temperatures has a flat minimum, depending upon volume: increase of energy during rarefaction is connected with the fact that for large dimensions of cell, electrons, due to presence of temperature and "thermal"

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*Even before the work of Latter, a number of authors [33] tried to consider by method of perturbation theory a temperature correction to solutions for zero temperature. However, such a procedure entails numerical calculations which are not much less complicated, than solution of exact equations, and encompasses a temperature range which is much narrower.

pressure, tend to occupy somewhat larger volume than in case of a cold cell, which leads to certain increase of potential energy.

As an example of temperature dependence of energy, we will indicate that energy of cell for one atom of iron, at normal density of solid iron, can be approximated in interval of temperatures from 20,000° to 30,000°K by interpolation formula

$$E = 0{,}865 T_{\text{эв}}^{1,6} \text{ ev/atom}$$

(from energy of cell there is eliminated energy E^{∞}; temperature is measured in ev).

At densities less than density of solid state, energy weakly depends on volume, roughly speaking, as $E \sim V^{0.15}$. In order to obtain total energy and pressure of substance, to electron components corresponding to atomic cell E and P it is necessary to add nuclear components (see beginning of § 13), i.e., to assume that

$$P_{\text{полн}} = P_{\text{я}} + P = n_{\text{я}} kT + P_e(V, T),\ P_e \equiv P,$$
$$E_{\text{полн}} = E_{\text{я}} + E = \frac{3}{2} kT + E_e(V, T) \text{ per atom; } E_e \equiv E.$$

For density equal to density of solid body, it is possible to somewhat improve these results by eliminating from pressure and energy quantities corresponding to cold cell of the same volume (since in reality pressure in real solid body at zero temperature is equal to zero), and adding to energy the binding energy of atoms of the solid body (heat of evaporation U)

$$P_{\text{полн}} = n_{\text{я}} kT + P_e(V, T) - P_e(V, 0),$$
$$E_{\text{полн}} = \frac{3}{2} kT + E_e(V, T) - E_e(V, 0) + U \text{ per atom.}$$

Thus energy is measured from normal state of solid body.

Literature

1. L. Landau and Ye. Lifshits. Statistical physics. State Technical Press, 1951.

2. I. N. Godnev. Calculation of thermodynamic functions according to molecular data. State Technical Press, 1956.

3. Tables of thermodynamic functions of air for temperatures from 6,000°K to 12,000°K and pressures from 0.001 to 1,000 atm, edited by A. S. Predvoditelev. Publishing House of Academy of Sciences of USSR, 1957; Tables of thermodynamic functions of air for temperatures from 12,000°K to 20,000°K and pressure from 0.001 to 1,000 atm, edited by A. S. Predvoditelev, Publishing House of Academy of Sciences of USSR, 1959.

4. V. V. Selivanov and I. Ya. Shlyapintokh. Journal of Physical Chemistry 32, 670 (1958).

5. Ye. V. Stupochenko, I. P. Stakhanov, Ye. V. Samuylov, A. S. Pleshanov, and I. B. Rozhdestvenskiy. Collection, Physical gas dynamics. Publishing House of Academy of Sciences of USSR, 1959, p. 3.

6. Ya. B. Zel'dovich. Journal of Physical Chemistry. 11, 685 (1938).

7. Atomic Energy Levels. Circular of the National Bureau of Standards. v. I, II, III, Washington, 1949-1957.

8. D. Kay and L. Libby. Handbook of the experimental physicist. IL, 1949.

9. E. Fermi, Nuovo Cimento 11, 157 (1934).

10. G. Ecker, Weizel, Ann. d. Phys., 17, 126 (1956); Seaton, Proc. Roy. Soc., A208, 408 (1951); Ehler, Weisaler, JOSA 45, 1035 (1955); E. Vitensee, Z. Astrophys., 28, 81 (1951).

11. B. L. Timan. ZhETF, 27, 708 (1954).

12. H. Margenau and M. Lewis. Rev. Mod. Phys., 31, 594 (1959).

13. L. P. Kudrin. ZhETF, 40, 1134 (1961).

14. S. W. Benson, Y. H. Buss, and H. Byers. IAS Paper. N 95, 14 (1959).

15. Yu. P. Rayzer. ZhETF, 36, 1583 (1959).

16. Ya. B. Zel'dovich and Yu. P. Rayzer. UFN, 63, 613 (1957).

17. Ya. B. Zel'dovich. Theory of shock waves and an introduction to gas dynamics. Publishing House of Academy of Sciences of USSR, 1946.

18. D. R. Davies. Proc. Phys. Soc., 61, 2, 105 (1948).

19. I. B. Rozhdestvenskiy. Collection, Physical gas dynamics. Publishing House of Academy of Sciences of USSR, 1959.

20. N. F. Gorban'. Collection, Physical gas dynamics. Publishing House of Academy of Sciences of USSR, 1959.

21. V. A. Prokof'yev. Scientific notes of Moscow State University. 172, Mechanics, 1954, p. 79.

22. E. L. Resler, S C. Lin, and A. Kantrowitz. J. Appl. Phys., 23, 1390 (1952); Selected translations, Mechanics, No. 5, 1953.

23. A. P. Sabol. Nat. Advis. Counc. Aeronaut. Thech. Notes, N 3091, 29 (1953).

24. S. R. Kholev. News of Institutes of Higher Learning. Physics, 4, 28 (1959).

25. R. H. Christian and F. L. Yarger. J. Chem. Phys., 23, 2042 (1955).

26. I. Sh. Model'. ZhETF, 32, 714 (1957).

27. R. G. Sachs. Phys. Rev., 69, 514 (1946).

28. V. A. Tsukerman and M. A. Manakov. ZhETF, 27, 391 (1957).

29. P. Gambosh. Statistical theory of the atom and its application. IL, 1951.

30. L. Landau and Ye. Lifshits. Quantum mechanics, I, State Technical Press, 1948.

31. R. Latter. Phys. Rev., 99, 1854 (1955).

32. M. Brachman. Phys. Rev., 84, 1263 (1951).

33. H. A. Bethe and R. E. Marshak. Astrophys., J. 91, 239 (1940); Feynman, Metropolis, Teller. Phys. Rev., 75, 1561 (1949); J. J. Gilvarry, Phys. Rev., 96, 934, 944 (1954); J. J. Gilvarry and G. H. Peebles, Phys. Rev., 99, 550 (1955).

34. A. I. Larkin. ZhETF, 38, 1896 (1960); A. A. Vedenov and A. I. Larkin, ZhETF, 36, 1133 (1959).

CHAPTER IV

SHOCK TUBES

§ 1. Use of Shock Tube for Study of Physicochemical Kinetics

In the preceding chapter were mentioned different physicochemical processes which occur in gases at temperatures of the order of a thousand or several thousand degrees and higher, such as excitation of molecular vibrations, dissociation of molecules, chemical reactions, ionization, emission of light. We considered the influence of these processes on thermodynamic properties of gases, absolutely not being interested by their kinetics, speeds of reactions, times of establishing thermodynamic equilibrium.

Meanwhile questions of kinetics have a large, frequently decisive value, if the over-all gas-dynamic process occurs so rapidly that thermodynamic equilibrium cannot be established, and state of gas particles is essentially unbalanced.

These questions are especially timely in connection with problems of entrance of rockets and artificial satellites into the atmosphere, supersonic flows in powerful jet engines, strong explosions, powerful electric discharges, etc.

In distinction from thermodynamic properties of gases, which are comparatively easily calculated by theoretical methods, our information about effective cross-sections of elementary processes and speeds of various physicochemical transformations is drawn mainly from experiment. The tool most convenient and widely applied at present for production in laboratory of high temperatures and investigation of physicochemical processes in gases is the shock tube. A shock tube serves for creation of a shock wave in the gas which heats the gas to the needed temperature.*

As we know, in a shock wave initially cold gas is practically instantly heated to a high temperature** which may be regulated, changing intensity of shock wave. Then in the heated gas particle begin different processes: excitation of molecular vibrations, dissociation, ionization, etc., role and speed of which depend on temperature (and density). Gradually these relaxation processes lead to establishment of thermodynamic equilibrium, corresponding to amplitude of shock wave. Thus, for a shock wave there exists an unbalanced shell (which it is possible to include in the idea of front of shock wave), where relaxation processes develop; this shell is also investigated by experiment. Theory permits connecting distribution of density and temperature in relaxation shell with speeds of reactions; therefore, measurement of distributions by experiment makes it possible to determine speed of relaxation processes. (In certain cases is possible direct recording of kinetics of reaction.)

We will deal in detail with the structure of relaxation layer in front of shock wave in Chapter VII. In Chapter VI will be considered different physicochemical processes occuring in heated gases, and estimates of their speed. Inasmuch as many actual data about speeds

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*There also exist other methods of obtaining shock waves: with the help of explosions, powerful electric discharges, etc.

**By "temperature" here is understood temperature of forward degrees of freedom of atoms and molecules.

are obtained with the help of the shock tube, it is expedient to see preliminarily how this important device works.

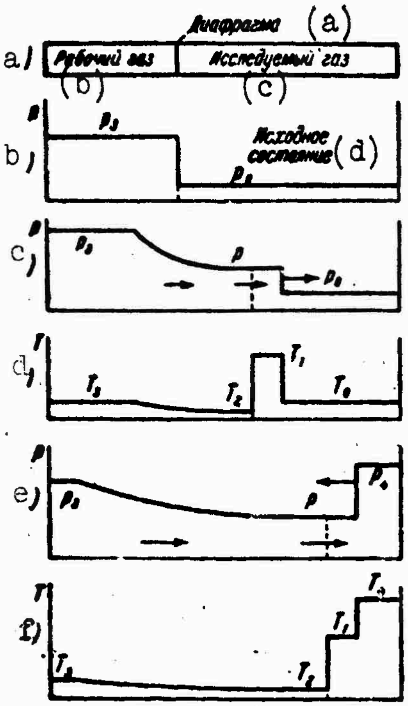

Fig. 4.1. Action of shock tube. a) diagram of tube before operation; b) profile of pressure before breaking of diaphragm; c), d) profiles of pressure and temperature in certain moment t_1 after breaking of diaphragm; e), f) profiles of pressure and temperature at time t_2 after reflection of shock wave from closed end of pipe. All profiles are given schematically. Arrows for shock waves show direction of propagation of shock wave. Other arrows show direction of motion of gas. KEY: (a) diaphragm; (b) working gas; (c) investigated gas; (d) initial state.

Let us stress that our account, pursuing a purely auxiliary purpose, will be extraordinarily short. It in no way reflects the real volume of experimental work which is truly huge. For more detailed familiarization with questions of construction and work of shock tubes, and also with experimental methods of investigations and measurements of different magnitudes, it is possible to recommend survey articles [1, 2] and books [3, 4]. In the same place the reader will also find reference to original works. Here these references are not numerous and have a more or less random character.

We will not remain on other methods of obtaining high temperatures (see [16]). Let us note only the very interesting works of Yu. N. Ryabinin [17] on adiabatic compression of gases. Gas in a pipe was compressed by a "flying" piston hundreds of times up to pressures in 10,000 atm. and adiabatically was heated up to temperatures ~9000°K. With the help of installation he created, Ryabinin studied thermodynamic and optical properties and electrical conductivity of high-heated gases.

§ 2. Principles of Action

A shock tube is a long pipe, usually round or of a right-angle cross section, which is divided by a thin diaphragm into two parts. One of them, the chamber of low pressure, is filled by the investigated gas. Into the second part, the chamber of high pressure, is forced the working gas. Dimensions of the tube are different. Usually its length is several meters, but the internal diameter is of the order of several centimeters. The length of the chamber of low pressure is a few times larger than the length of the chamber of high pressure. Pressure of investigated gas, as a rule, does not exceed atmospheric, and most frequently is lower, of the order of several centimeters of mercury. In the chamber of high pressure it is attempted to create a possibly larger pressure, of the order of several tens or hundreds of atmospheres.

At the needed moment the diaphragm, with the help of a special device, quickly bursts and the strongly compressed working gas rushes into the chamber of low pressure. Along the investigated gas spreads a shock wave, but along the working gas runs a wave of rarefaction. Profiles of pressure before and after break of diaphragm, and also profile of temperature after break of diaphragm are schematically shown in Fig. 4.1.

On the figure are not shown the parts of distribution of magnitudes in front of shock wave, which is represented in the form of a "classical" shock wave. After the shock wave reaches the end of the tube, usually a closed motionless cover, it is reflected and flows toward the working gas. Pressure and temperature in the reflected shock wave sharply jump as compared to values in the incident wave. Gas in the

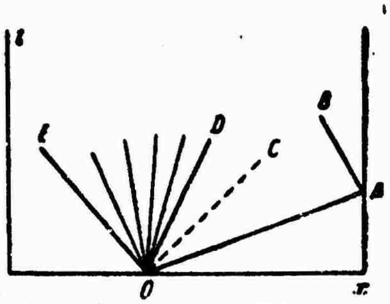

Fig. 4.2. x,t-Diagram for motion in shock tube, shown in Fig. 4.1. OA — shock wave, OC — contact discontinuity, fan between OE and OD — wave of rarefaction in working gas, AB — reflected shock wave.

reflected shock wave is motionless with respect to walls of pipe. x, t-Diagram of process is shown in Fig. 4.2.

§ 3. Elementary Theory of Shock Tube

Parameters of incident shock wave are easy to estimate, considering the collapse of the arbitrary initial break (see § 24, Ch. I). We will consider for simplicity that investigated and working gases possess constant adiabatic indices γ and γ' correspondingly, we will consider only strong shock waves.* Let us ascribe to the magnitudes in undisturbed investigated gas the index "0", the index "1" to the magnitudes after front of shock wave, the index "2" to the magnitudes in the working gas, having passed through the wave of rarefaction, and the index "3" to magnitudes in the undisturbed wave of rarefaction working gas.

By the formulas of (1.111) for a strong shock wave we have

$$\rho_1 = \frac{\gamma+1}{\gamma-1}\rho_0, \quad p_1 = \frac{2}{\gamma+1}\rho_0 D^2, \quad u_1 = \frac{2}{\gamma+1} D, \quad p = \frac{R}{\mu}\rho T \tag{4.1}$$

(μ — molecular weight of investigated gas).

On contact boundary between the two gases pressure and speed are continuous, so that $p_2 = p_1 = p$, $u_2 = u_1 = u$ (density and temperature on contact experience a discontinuity). The contact boundary, which moves with speed u, serves as a "piston", pushing the shock wave. By the known formula (see § 10 Ch. I) speed of working gas, having passed through the wave of rarefaction, equals

$$u = \frac{2}{\gamma'-1}(c_3 - c_2) = \frac{2}{\gamma'-1} c_3 \left(1 - \frac{c_2}{c_3}\right), \tag{4.2}$$

where speed of sound c_2 and c_3 are connected by the condition of

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*Is assumed also that the mass of the diaphragm may be disregarded, i.e., times are considered when the shock wave encompasses a sufficiently large mass of investigated gas.

adiabacity of expansion:

$$\frac{c_2}{c_3}=\left(\frac{p}{p_3}\right)^{\frac{(\gamma'-1)}{2\gamma'}}.$$

Expressing $p = p_1$ by $u = u_1$ according to the formulas of (4.1) we will obtain an equation from which can be found speed of "piston" at known initial values of parameters:

$$\frac{u}{c_3}=\frac{2}{\gamma'-1}\left\{1-\left[\frac{\gamma'(\gamma+1)}{2}\frac{\rho_0}{\rho_3}\frac{u^2}{c_3^2}\right]^{\frac{\gamma'-1}{2\gamma'}}\right.. \tag{4.3}$$

Speed of sound c_3 equals $c_3=(\gamma'\frac{R}{\mu'}\ T_3)^{1/2}$, where μ' is molecular weight of working gas. Intensity of shock wave is completely determined by speed of "piston" u. In particular, temperature after the front equals $T_1=\frac{\gamma-1}{2}\ \mu u\ \frac{2}{R}$.

The most powerful shock wave, other things being equal, will be formed if ratio of initial densities ρ_0/ρ_3 is small, so that the working gas, after break of diaphragm, flows practically into a vacuum, with maximum speed of outflow

$$u_{max}=\frac{2}{\gamma'-1}c_3=\frac{2}{\gamma'-1}\left(\gamma'\frac{R}{\mu'}T_3\right)^{\frac{1}{2}}. \tag{4.4}$$

The corresponding upper limit of temperature for the front of the shock wave equals

$$T_{1max}=\frac{2\gamma'(\gamma-1)}{(\gamma'-1)^2}\frac{\mu}{\mu'}T_3. \tag{4.5}$$

From the last formula it is clear that for creation of high temperatures it is necessary to use a light working gas, while the highest temperatures appear in heavy monatomic gases (the less the heat capacity, the bigger the magnitude $\gamma - 1 = R/c_V$, which is in the numerator of formula (4.5)).

The most profitable of all to use as a working gas is hydrogen ($\mu' = 2$, $\gamma' = 7/5$, $T_{1\ max} = 8.75(\gamma - 1)\mu T_3$); helium is also used

($\mu' = 4$, $\gamma' = 5/3$, $T_{1\ max} = 1.87(\gamma - 1)\mu T_3$).

Achievement of highest possible speed (4.4) requires an exceptionally small ratio of initial densities of gases ρ_0/ρ_3 (extraordinarily large pressure drop p_3/p_0). Under real values of pressure drop the investigated gas renders an essential "resistance" to the outflow of working gas and speed u, calculated by equation (4.3), turns out to be a few times less than speed of outflow into the vacuum. Temperature in the shock wave is lowered still more sharply.

Let us consider a specific example. Let us assume that hydrogen serves as the working gas and argon is investigated ($\mu = 40$, $\gamma = 5/3$). Initial temperatures of both gases are identical and are equal to room temperature: $T_0 = T_3 = 300^{\circ}K$. Ratio of initial pressures $p_3/p_0 = 7600$, we will say, $p_0 = 5$ mm Hg, $p_3 = 50$ atm. We obtain: u = 3.9 km/sec, D = 5.2 km/sec, Mach number $M = \frac{D}{c_0} = 16$, $T_1 = 41T_3 = 12{,}300^{\circ}K$, $p_1 = 320p_0 = 2.1$ atm. Upper limit of speed $u_{max} = 9.4$ km/sec.*

In fact, temperature in shock wave will be somewhat lower than $12{,}300^{\circ}K$, since with such a temperature consumption of energy on ionization of argon already plays a certain role, which somewhat lowers effective adiabatic index of argon γ. For more exact calculations it is necessary to use the actual shock adiabat of gas, taking into account ionization. Values of speed of gas u, calculated by equation (4.3), and also values of speed of front, pressure, internal energy in shock wave are little sensitive to assumptions relative to thermodynamic properties of the investigated gas. Calculation of temperature without taking into account consumption of energy on ionization, dissociation, etc. can give strongly oversized figures.

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*Calculation of $T_{1\ max}$ by formula (4.5) which for adiabatic index $\gamma = 5/3$ gives $70{,}000^{\circ}K$, has no meaning, since at such high temperatures the essential role played by ionization and actual temperature is much lower.

During investigation of air in a shock tube with hydrogen as the working gas speeds of front up to 4 km/sec are obtained. (Mach number of order 12) and temperature after front of shock wave of the order of 4000°K. There are different methods of increase of effectiveness of shock tubes, making it possible to increase somewhat the parameters of shock wave. In particular, it is profitable to increase initial temperature of working gas T_3 (see formula (4.5)). For this an explosive mixture of hydrogen with oxygen is frequently used as the working gas (the mixture is usually diluted by a light neutral gas — helium). At the needed moment the mixture is ignited and as a result of the reaction the working gas is heated. In such a way we obtain in air speeds D of the order of 5 km/sec (Mach number of order 15) and temperatures of the order of 6000°K. Constructions of shock tubes have been developed with a variable cross-section and others (see [4]).

Let us calculate now parameters of reflected shock wave, as before considering that heat capacity and adiabatic index are constant. To parameters of the reflected wave we will ascribe the index "4," and a "1" to parameters of the incident wave, as also earlier. Using formula (1.69), connecting difference of pressures, specific volume and speeds with respect to both sides of front of shock wave. Difference of speeds, which is speed of gas after front with respect to gas before front, in incident and reflected waves is identical. Assuming that the incident wave is strong, we will obtain hence equation

$$u^2 = (p_4 - p_1)(V_1 - V_4) = p_1(V_0 - V_1).$$

Equation of shock adiabat (1.76) for reflected wave (which is not strong) has the form

$$\frac{V_4}{V_1} = \frac{(\gamma+1)p_1 + (\gamma-1)p_4}{(\gamma-1)p_1 + (\gamma+1)p_4}.$$

Noticing that $V_0/V_1 = (\gamma + 1)/(\gamma - 1)$ and excluding from these two equations V_4/V_1, we will find pressure ratio on front of reflected wave P_4/P_1, after which we will calculate density ratio and temperatures. We obtain

$$\frac{p_4}{p_1}=\frac{3\gamma-1}{\gamma-1},\quad \frac{\rho_4}{\rho_1}=\frac{\gamma}{\gamma-1},\quad \frac{T_4}{T_1}=\frac{3\gamma-1}{\gamma}. \tag{4.6}$$

During numerical estimation it is necessary to show caution. The fact is that in reflected wave temperatures usually so are high that heat capacity of gas due to dissociation, ionization, etc., is not constant. Strictly speaking, parameters of reflected wave should be calculated using real thermodynamic functions of gas. However, for a rough estimate it is possible to use formulas (4.6), selecting for the adiabatic index a certain effective value. In rarefied gas in the region of dissociation or ionization it is possible to take for an estimate, for instance, $\gamma = 1.20$. This gives: $p_4/p_1 \approx 13$, $\rho_4/\rho_1 \approx 6$, $T_4/T_1 \approx 2.17$. In heavy monatomic gases tens of thousands of degrees, can be obtained in reflected shock wave. In air at initial pressure $p_0 = 10$ mm Hg and speed of incident wave $D \approx 5$ km/sec when $T_1 \approx 5800^{\circ}$K, $\rho_1/\rho_0 \approx 10$, in reflected wave $T_4 \approx 8600^{\circ}$K, $\rho_4/\rho_1 \approx 7$ (these data are obtained taking into account real thermodynamic properties). The real process in a shock tube is much more complicated than is sketched by the idealized system given above. The shock wave becomes stationary not immediately after the diaphragm breaks, but only after a certain time. Friction against walls, interaction with boundary layer, especially in reflected shock wave, irregularity of heating with respect to cross-section of tube, loss of energy through walls and on radiation (at very high temperatures), mixing of gases near contact discontinuity and many other effects play a role (see in reference to this [2, 4, 5]; in the same place are references to many original works).

§ 4. Electromagnetic Shock Tubes.

Shock tubes, in which a shock wave in the investigated gas is obtained during a sudden expansion of initially compressed working gas, are widely used for investigation of different high-temperature processes. However, maximum speeds of the shock wave (Mach number), and consequently also temperatures which are attained even in improved constructions based on the shown principle, are very limited.

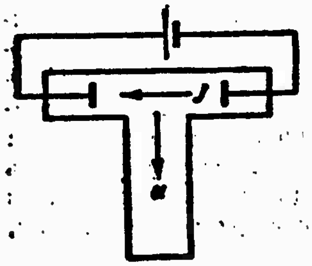
Fig. 4.3. Diagram of T-form of Fowler tube.

Recently new types of shock tubes were proposed, at the basis of which lie other principles. In these devices, which are frequently called electromagnetic or magnetic shock tubes, for creation of intense shock waves effects of heating of gas during an electric discharge and acceleration of it under action of magnetic intensities are used. The early construction of Fowler and his colleagues [6] is the T-form tube shown in Fig. 4.3. The tube is filled by the investigated gas under low pressure, of the order of a millimeter of mercury. Into the cross beam of the "T" are introduced electrodes and through the gas is discharged a capacitor battery. Gas in the discharge is rapidly heated to a high temperature and under the action of high pressure with great speed spills into the "vertical" tube, pushing before itself a shock wave.

In distinction from Fowler tube, where electric discharge is used as a means of rapidly heating the gas, in the T-form tube built by Kolb [7] for acceleration of gas — plasma. The phenomenon of electromagnetic interaction of currents is used. A busbar, along which flows a return current in the electrical discharge circuit, maxmally nearing the discharge part of the tube, as was shown in Fig. 4.4. As is known, parallel conductors with oppositely directed currents are repelled from each other. This may be considered as the result of influence of the magnetic field of one current on the conductor with the other current. The force acting per unit of volume of conductor with the current, is determined by vector product of density of current j and magnetic field strength **H**: $f = \frac{1}{c}[j\,\mathbf{H}]$ (permeability of plasma is very close to unity). This force is perpendicular to directions of current and magnetic field. In this case the magnetic field of return current, current along the busbar repels the plasma with a discharge current flowing along it in the direction of the vertical tube, additionally accelerating it. As is said, a "magnetic piston" acts on the plasma. The plasma spills into the vertical tube with a still higher speed, creating in the latter an even more powerful shock wave than in the absence of a magnetic field. Dimensions of magnetic shock tube are small: radius is approximately 1.5 cm; length of vertical part is 12 cm. In one of the typical experiments of Kolb, a tube was filled by deuterium with an initial pressure of 0.7 mm Hg. Capacitance of capacitor battery was $C = 0.52$ μf; it was charged to $V = 50$ kv. As an oscillogram of discharge current showed frequency of discharge was equal to $\nu = 700$ kc. With these parameters was attained maximum speed of shock wave, $D = 90$ km/sec (at a distance of 3.5 cm from the discharge part of the tube). The wave is weakened according to propagation, for instance, at a distance of 9 cm its speed drops to 75 km/sec. Temperature after the front of the shock wave at $D = 90$ km/sec equalled approximately 120,000°K.*

With a simple estimate we will ascertain that magnetic intensity with the shown parameters indeed can accelerate the plasma to such a

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*This temperature is calculated with respect to speed of front with the help of shock adiabat taking into account effects of dissociation, but without taking into account radiation flux from front, since it is small due to transparency of gas.

high speed. Without taking into account damping (which is small) discharge current from moment of rupture is changed according to the sinusoidal law $I = I_{max} \sin \omega t$, where $\omega = 2\pi\nu$, and $I_{max} = V(C/L)^{1/2} = VC\omega$ (L is self-inductance of circuit, and in this case equals 0.1 millihenry). Maximum current equals $I_{max} = 115{,}000$ amp $= 1.5 \cdot 10^5$ c/10 units of the CGS electrostatic system. Current I, flowing along the busbar, creates at distance r from it magnetic field $H = 2I/cr$. As average distance between busbar and plasma it is possible to take radius of tube. Magnetic field acts on plasma as a piston with pressure $H^2/8\pi$. Speed u, which plasma obtains under action of such pressure, is determined by evident relationship $H^2/8\pi \approx \rho u^2$, where ρ is density; hence $u = H/\sqrt{8\pi\rho} = I/cr\sqrt{2\pi\rho}$. As I we will take average current $I = (\overline{I^2})^{1/2} = I_{max}/\sqrt{2}$.

Putting in formula for speed $r = 1.5$ cm, $\rho = 0.74 \cdot 10^{-7}$ g/cm^3 (this is the density of deuterium under a pressure $p_0 = 0.7$ mm Hg and room temperature) and magnitude of current, we will obtain $u = 80$ km/sec. Thus, the magnetic piston accelerates the plasma to a speed of the order of the observed ($D_{max} \approx 90$ km/sec). Let us note that time of action of magnetic piston, which is of the order $t \approx r/u \approx 1.9 \cdot 10^{-7}$ sec, is less than a quarter of the period of discharge $T/4 \approx 1/4\,\nu = 3.6 \cdot 10^{-7}$ sec. The whole process of acceleration of plasma occurs in the first quarter of the period of discharge, while the current does not grow to maximum value. In calculation which was made, we disregarded acceleration owing to purely thermal expansion of plasma heated by discharge current. Estimates show that indeed the basic role in acceleration is played by magnetic pressure, but not thermal pressure. For an increase of magnetic pressure acting on the plasma, in certain experiments to the magnetic field of the return current (which for $I = \frac{I_{max}}{\sqrt{2}} = 80{,}000$ amp and r = 1.5 cm equalled approximately 11,000 oe) was added still an external magnetic field of the same direction (~15,000 oe). In the Kolb T-form tube it is very important to obtain a high speed of build-up of current and a large amplitude of current (high frequency of discharge), i.e., it is necessary to take special measures for maximum decrease of self-inductance of circuit.*

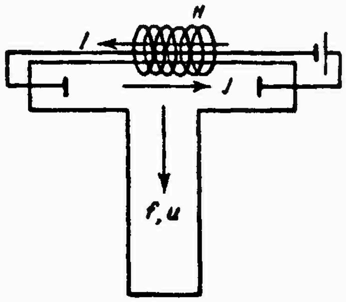

Fig. 4.4 Diagram of electromagnetic Kolb tube.

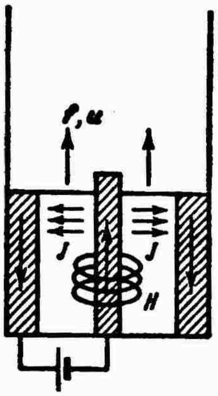

Fig. 4.5. Diagram of Kolb and Poltavchenko tube. Electrodes are shaded.

By the principle of the "magnetic piston" also acts the other tube, built by S. P. Poltavchenko and D. S. Poltavchenko [9], whose diagram is shown in Fig. 4.5. The discharge current flows in a radial direction between the electrodes, one of which is a rod located on axis of tube, and the other is a cylinder near surface of tube. Radial discharge current interacts with concentric magnetic current field, flowing along the central electrode. A pondermotive force is directed along axis of tube and accelerates plasma in this direction. Along the tube spreads a shock wave. A characteristic is ejection of plasma from interelectrode region, breaking away of it from "bottom" of tube under the influence of magnetic field, which acts like a piston.

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*Let us indicate [8], whose authors obtained intense shock waves in a T-form tube filled by hydrogen and helium, and investigated the glow of heated gas in filaments.

Experiments were made in air. The most intense shock wave with Mach number $M \approx 250$, $D \approx 80$ km/sec, $T_1 = 130{,}000^{\circ}K$ was obtained with the following parameters: $C = 2400$ mf, $V = 5$ kv, $I \approx 560{,}000$ a (the tube was made from plexiglas and had a diameter from 2 to 5 cm and a length from 50 to 90 cm). The wave rather rapidly attenuates during propagation along pipe. Weakly attenuating shock waves, but then smaller amplitude, ($D < 10$ km/sec) are obtained on the device of S. R. Kholev and L. I. Krestnikova [10].

Principle of action of the above tube of S. R. Kholev and D. S. Poltavcheko has much in common with principle of action of the doughnut tube built by Patrick [11].

Josephson [12] described a tube with a conical hood. To the cylindrical pipe is joined a conical hood (Fig. 4.6). On its end is located central electrode. The second electrode is the ring on the joint of cylindrical and conical parts of tube. Along the generatrix of the cone go busbars for return current. During discharge there occurs magnetic compression of plasma to the axis — "pinch effect" — where radial compression starts near central electrode and gradually includes layers closer to the central. Then the accelerated plasma is ejected into a cylindrical tube, forming a shock wave in it. In [13] such a tube was used for acceleration of strongly rarefied air to speeds of the order of 12 km/sec ($M \approx 40$, $T_1 \approx 12{,}000^{\circ}K$) and investigation of flow around models simulating rocket heads.

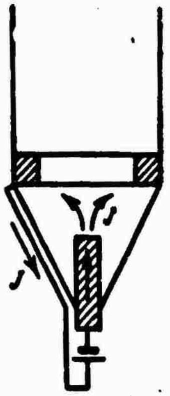

Fig. 4.6. Diagram of tube with conical head. Electrodes are shaded.

More specifically, questions of construction of electromagnetic shock tubes and work with them can be found in the collection of translations [14].

§ 5. Methods of Measurements of Different Magnitudes

Up to the present time there have been developed and widely used various methods of observation of fast-flowing processes in shock tubes and measurement of different magnitudes: speed of front of shock wave, density, temperature, and others. A description of these methods and an account of results obtained with their help is the subject of extensive literature. Many questions can be met in [3, 4] and surveys [1, 2]; in the same place are numerous references to journalistic articles.

Here we will not remain on a detailed consideration of methods of experiment and we will only briefly enumerate the basic ones. We hold the basic classification of methods accepted in survey [2].

1. High-speed photographic survey. The gas-dynamic process can be photographed either thanks to intrinsic radiation of gas heated to a high-temperature, or in light of an outside source. Chambers have been developed and applied which permit filming of the rapid processes with a frequency up to a million frames per second.* Widely applied also is the method of photo-scanning at which a beam of light, being reflected from a revolving mirror, continuously runs along the film, so that a moving luminescent object (let us say, front of shock wave) describes on the film a continuous slanted line. By slope of the line one can determine speed of object.

2. Measurement of density. Measurement of distribution of density of gas in an unbalanced layer after the shock wave has an especially important value, since distribution of density is connected with speeds of relaxation processes (see Ch. VII). Namely, in such a way were

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*For references to works of Soviet scientists and designers — creators of unique high-speed chambers, see in Chapter XI.

basically determined speeds of excitation of vibrations and dissociation of molecules at high temperatures.

For measurement of distribution of density mainly the interference method is applied, at the basis of which lies the fact that the refractive index of a gas is changed with a change of its density. On the change of refractive indices during motion of compressible gas are based other important optical methods of observation of field of flow: the schlieren method and the shadow method. However, the most exact quantitative data on distribution of density is given by the interference method.*

In the works of Corning and others [3] distribution of density in front of weak shock waves was determined according to reflection of light from surface of front. Initial density of gas was selected in such a manner that thickness of front of shock wave was comparable with wave length of light. Under this condition the coefficient of reflection depends on thickness of transition layer and distribution of density (i.e., refractive index) in it. Thus were measured thickness of front and speed of excitation of rotations of molecules in weak shock waves.

Distribution of density of gas was measured also according to scattering of electron beam, by absorption of x-rays.

3. <u>Measurement of concentration of components of gas</u>. In a number of cases, when in an unbalanced layer after the shock wave there is dissociation of molecules or a chemical reaction, it is possible to watch directly for change of concentration of specific particles. This is usually possible, if any particles possess absorption of light, sharply expressed as compared to other particles. Thus, for instance,

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*The shown optical methods, in which light is used from an outside source, usually are applied at not too high a temperature, when intrinsic radiation of the heated gas is small.

was studied the dissociation of molecules of bromine and iodine in a shock wave, dissociation of molecules of oxygen, etc. Molecules of bromine and iodine strongly absorb visible light, whereas their atoms do not absorb; molecules of oxygen possess characteristic system of absorption bands in ultraviolet region (see Ch. V).

4. Measurement of emission and absorption of light. In many works spectral measurements were made of emission rate of light by gas heated from a shock wave. Knowing density of gas and temperature, it is possible thus to determine radiating ability at various temperatures and in various sections of the spectrum. Light is usually registered by photographic methods or with the help of photomultipliers. According to radiating ability, using Kirchhoff's law (see Ch. V) coefficient of absorption of light in heated gas can also be found. Coefficients of absorption sometimes are also measured directly, according to weakening of beam of light from outside source during passage through gas.

5. Measurement of temperature. For measurement of high temperatures optical methods are most frequently applied. Literature on methods of optical pyrometry is huge. We recommend, in particular, collection of translation [15]; see also survey [16].

6. Measurement of concentration of electrons and electrical conductivity. For measurement of degree of ionization of gas and concentration of electrons in shock wave the probe method of Langmuir, which is applied during the study of gas discharges, is frequently used. Applied also is the method of absorption and reflection of microradiowaves. Concentration of electrons is measured also according to glow of gas (for instance, intensity of recombination glow is proportional to the square of concentration of electrons). Magnetic methods, in particular, based on effect of displacement of moving

plasma of an external magnetic field are applied; displacement depends on electrical conductivity. Determining electrical conductivity, it is possible to calculate concentration of electrons.

7. Measurement of pressure. Pressure most frequently is measured with the help of piezoelectric transducers with a sensing device from barium titanate.

8. Measurement of speed of front of shock wave. The simplest of all to measure is speed, recording by one or another method the moments of passage of a shock wave of specific cross sections (at known distances from each other) in a tube. For registration piezopressure transducers, ionization transducers, different electromechanical transducers, and others, are used.

Very high speeds which are obtained in electromagnetic shock tubes, are usually measured with the help of photo-scanning (see paragraph 1).

Literature

1. S. S. Penner, F. Harshbarger, and V. Valley. Problems of rocket. tech., No. 6 (1958); No. 1 (1959).

2. S. A. Losev and A. I. Ositpov. UFN, 74, 3, 393 (1961).

3. Physical measurements in gas dynamics and during burning. Translation of 9th volume of the series "Aerodynamics of high speeds and jet enginneering," IL, 1957.

4. Shock tubes. Collection of translations of articles edited by Kh. A. Rakhmatullin and S. S. Semenov, IL, 1962.

5. R. A. Strelow and A. Kochen. Problems of rocket. tech., No. 9 (1959).

6. R. G. Fowler, W. R. Atkinson, W. D. Compton, and R. J. Lee. Phys. Rev., 88, 137 (1952); R. G. Fowler, W. R. Atkinson, and L. W. Marks. Phys. Rev., 87, 966 (1952).

7. A. C. Kolb. Phys. Rev., 107, 345, 1197 (1957).

8. W. Wiese, H. F. Berg, and H. R. Griem. Phys. Rev., 120, 1079 (1960).

9. S. R. Kholev and D. S. Poltavchenko. DAN, 131, 1096 (1960).

10. S. R. Kholev and L. I. Krestnikova. News of Institutes of Higher Learning, Physics, 1, 29 (1960).

11. R. M. Patrick. Phys. Fluids 2, 599 (1959).

12. V. Josephson. J. Appl. Phys., 29, 30, 1958.

13. R. V. Zimmer. Problems of rocket. tech., No. 4, 44 (1960).

14. Moving plasma. Collection of translations. IL, 1961.

15. Optical pyrometry of plasma. Collection of translations. IL, 1960.

16. V. Lochte-Holtgreven. UFN, 72, No. 3 (1960).

17. Yu. N. Ryabinin. Gases at large densities and temperatures. Fizmatgiz, 1959.

CHAPTER V

ABSORPTION AND EMISSION OF RADIATION IN GASES AT HIGH TEMPERATURES

§ 1. Introduction. Types of Electron Transfer

In Chapter II it was shown that the basic optical characteristic of a gas, which determines degree of blackness of a heated body, intensity and radiation spectrum, energy balance of substance in conditions of radiant heat exchange, is the coefficient of absorption of light.* Knowing the coefficient of absorption, with the help of Kirchhoff law, which serves as an expression of the general principle of detailed equilibrium, light emissivity of a substance can also be found.

In § 2 Chapter II was given a short survey and classification of different mechanisms of absorption and radiation.

In accordance with the general scheme of possible energy states of the atomic system, the simplest of which is a system from one proton and one electron, in the bound state forming an atom of hydrogen, all possible electron transfers accompanying absorption and radiation of light were subdivided into three types. Thus:

1) free-free transfers (bremsstrahlung and absorption of light);

2) bound-free transfers (photoelectric absorption);

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*We recall that, speaking of "light," "light quanta," "optical" properties, we consider radiation of any frequencies, and not only those belonging to the visible part of the spectrum.

3) bound-bound (discrete) transfers.

Free-free and bound-free transfers lead to formation of a continuous (solid) absorption spectrum and radiation of light.

Bound-bound transfers in atoms give a line spectra. As a result, bound-bound transitions in molecules form band spectra. Band spectra consist of a great number of spectral lines closely located one to another with respect to frequency. In certain conditions the separate lines are so closely adjacent that they even partially overlap and an almost continuous (quasi-continuous) spectrum is obtained.

From the point of view of energy, there is a fundamental interest in continuous (quasi-continuous) spectra.

Let us imagine, for instance, a body heated to constant temperature T. If it is an ideal black body, then from its surface emerges a radiation flux with plank distribution with respect to the spectrum. A spectral flux as a function of frequency ν is shown in Fig. 5.1 by the dotted curve. The area bound by this curve gives total quantity of radiant energy emitted from 1 cm^2 of the surface of a body in 1 sec and equal to σT^4. Let us assume now that a substance, absolutely transparent in the continuous spectrum, absorbs and radiates only line spectrum, while in frequency lines radiation is in thermodynamic equilibrium with substance. Spectral radiation flux from the surface of a body is shown now by a system of separate narrow lines whose height corresponds to Planck function, as is shown in Fig. 5.1 by solid curves. The total quantity of radiant energy outgoing from 1 cm^2 of the surface of a body in 1 sec is numerically equal to the shaded area of these lines, which due to small width of lines, is much less than total plank flux σT^4. Losses of energy of body on radiation, and also brightness of glow of surface in the considered case is much less than if the spectrum was continuous.

Exactly as in many cases, line spectra play a small role as compared to continuous spectra, in transfer of radiant energy inside a body. Therefore, basic attention in this chapter will be allotted not to line spectra, but to continuous and quasi-continuous molecular spectra.

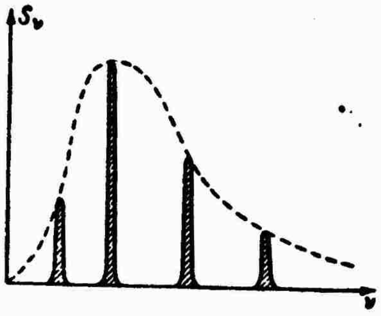

Fig. 5.1. Emission spectrum of a heated body, absolutely transparent in the continuous spectrum, but opaque in lines. Dotted curve corresponds to plank spectrum at a given temperature.

At high temperatures, when molecules are dissociated and a gas consists of atoms, and at still higher temperatures when a gas consists of ions and electrons, a continuous spectrum of absorption and emission appears as a result of bound-free and free-free transfers. Calculation of probabilities of electron transfers, with whose help can be found coefficients of absorption (and emission) of light in the case of many-electron atoms (complex atomic systems), constitutes a very difficult quantum-mechanical problem. It requires special consideration in every specific case, for every atom or ion and even for every quantum state of system. Such calculations are made only for a few particular cases.

A comparatively simple calculation can be conducted only for the simplest, hydrogen-like system, i.e., for transfers of a single electron in a Coulomb field of positive charge Ze. Practically, even in examining absorption and emission of light in gases consisting of complex atoms or ions, frequently it is necessary to use formulas derived for hydrogen-like systems.

Here the atom or ion is in the form of some "atomic remainder" with positive point charge Ze, in the field of which moves an "optical" electron, transient during absorption or emission of light quantum from one energy state to another. As will be shown below, in a number of practically important cases, such an approximation turns out to be to a certain degree justified.

During calculation of coefficients of molecular absorption usually it is possible to determine the coefficient as a function of frequency and temperature with an accuracy up to a certain factor – strength of oscillation for a given electron transition, which, as a rule, is found from experiment.

In subsequent paragraphs of this chapter we will consider in detail different mechanisms of absorption and emission of light in gases at high temperatures and the calculated corresponding coefficients of absorption. We will be interested basically in the physical side of matter, not remaining in detail on different approximate methods of improvement of calculation formulas for coefficients of absorption.

Very frequently in absorption and emission of light in gas during all given conditions a whole series of mechanisms participates. All of them act independently from each other. Total absorption coefficients and radiating abilities in every spectral section are composed of magnitudes, corresponding to different mechanisms. Therefore, consecutive and independent consideration of separate mechanisms is fully natural. At the end of the chapter, as the most important example of such joint action of many mechanisms, from a practical point of view, the optical properties of heated air will be considered.

1. <u>Continuous Spectrum</u>

§ 2. Bremsstrahlung of Electron in Coulomb Field of Ion

As is known from classical electrodynamics, a free electron, moving in an external electrical field, let us say, in a Coulomb field of an ion with positive charge Ze, radiates light. It loses part of its kinetic energy, and is "braked," which is why such radiation is called braking.*

The quantity of radiant energy S, emitted by an electron in 1 sec is determined by its acceleration w;

$$S=\frac{2}{3}\frac{e^2}{c^3}w^2. \tag{5.1}$$

Total radiation for the whole electron transit time past the ion equal to the integral with respect to time from this expression:

$$\Delta E=\int_{-\infty}^{\infty}S\,dt=\frac{2}{3}\frac{e^2}{c^3}\int_{-\infty}^{\infty}w^2\,dt. \tag{5.2}$$

Spectral composition of radiation can be found by expanding g-vector w into a Fourier integral and putting the expansion in formula (5.2).

We will obtain

$$\Delta E=\frac{8\pi}{3}\frac{e^2}{c^3}\int_{0}^{\infty}w_\nu^2\,d\nu=\int_{0}^{\infty}S_\nu\,d\nu, \tag{5.3}$$

where

$$w_\nu=\frac{1}{2\pi}\int_{-\infty}^{\infty}w(t)\,e^{-i2\pi\nu t}\,dt$$

is Fourier component of g-vector w(t).

Magnitude

$$S_\nu=\frac{8\pi}{3}\frac{e^2}{c^3}w_\nu^2 \tag{5.4}$$

constitutes the quantity of radiant energy of frequency ν, emitted during the transit of an electron past the ion and happening on a unit interval of frequencies.**

According to classical mechanics, in the absence of losses of

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*Ed. note. The Russian term for bremsstrahlung includes the word for "braking" or "decelerating," whereas the English term does not.

**In accordance with astrophysical traditions we will always use not angular frequency $\omega = 2\pi\nu$, but ordinary ν.

energy on radiation the free electron (sum of kinetic and potential energies of which is positive) flies past the ion along a specific hyperbolic orbit, characterized by impact parameter ρ, the meaning of which is clear from Fig. 5.2.

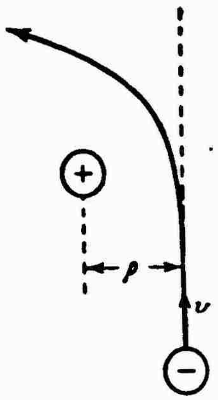

Fig. 5.2. Trajectory of electron during transit past positive ion.

The total quantity of radiated energy and spectral composition of radiation may be approximately calculated by the formulas of (5.2)-(5.4), taking as acceleration **w**(t) the magnitude corresponding to motion of electron without radiation.*

Let us assume that onto an ion from infinity drops a parallel beam of electrons whose initial speed on infinity equals v and density N_e is constant (electron stream equals $N_e v$). Through an elementary ring with an area of $2\pi\rho\, d\rho$ near the ion in 1 sec pass $N_e v \cdot 2\pi\rho\, dp$ electrons. Each of them radiates an energy of ΔE erg. Radiation of these electrons in 1 sec equals $\Delta E N_e v \cdot 2\pi\rho \cdot d\rho$ erg/sec. Radiation in 1 sec of electrons passing the ion along all possible orbits, will be obtained if one integrates this expression with respect to ρ from 0 to ∞. Total energy content of radiation calculated on one ion and a single electron stream $N_e v = 1\ \mathrm{cm}^{-2}\ \mathrm{sec}^{-1}$, is

$$q = \int_0^\infty \Delta E \cdot 2\pi\rho\, d\rho\ (\mathrm{erg \cdot cm^2}). \qquad (5.5)$$

It is possible to speak also about content of energy radiated in an interval of frequencies from ν to ν + dν, about so-called effective radiation $dq_\nu \left(\int_{\nu=0}^{\nu=\infty} dq_\nu = q_\nu\right)$. In accordance with determination (5.3) effective radiation, i.e., content of energy radiated in interval of frequencies dν from calculation on one ion and single electron stream

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*This corresponds to the assumption about the fact that radiation is small.

equals

$$dq_\nu = d\nu \int_0^\infty S_\nu 2\pi\rho\, d\rho \; (\text{эрг}\cdot\text{см}^2). \tag{5.6}$$

By effective radiation is determined spectral radiating ability of a substance due to bremsstrahlung.

If in 1 cm^3 there are N_+ ions of a specific kind and dN_e electrons with velocities from v to v + dv, then energy content in interval of frequencies from ν to $\nu + d\nu$, emitted in 1 sec in 1 cm^3 as a result of the deceleration of these electrons in a field of ions, equals $N_+ \, dN_e v \cdot dq_\nu$ $erg/cm^3 sec$.

Let us estimate effective electron emission in a Coulomb field of an ion. If electron is at distance r from the ion (radius vector **r**), from the ion force $-Ze^2\mathbf{r}/r^3$ acts on it. Acceleration caused by this force is equal to $\mathbf{w} = -Ze^2\mathbf{r}/r^3 m$, where m is mass of electron. Let us assume that the electron possesses initial velocity v and flies past the ion on impact parameter ρ. Time of action of force is of the order $t \sim \rho/v$, and acceleration during this time is of the order $w \sim Ze^2/\rho^2 m$. In the expansion of vector of acceleration into a Fourier integral a basic role is played by frequency of the order $\nu \sim 1/2\pi t \sim v/2\pi\rho$.* It is possible to say that frequency ν basically is radiated by those electrons which fly past the ion on impact parameter $\rho \sim v/2\pi\nu$, and frequencies in interval from ν to $\nu + d\nu$ are emitted mainly by electrons with impact parameters included in the interval $d\rho \sim \frac{v}{2\pi\nu^2} d\nu \sim 2\pi \frac{\rho^2}{v}\, d\nu$.

Energy emitted by each such electron is of the order

$$\Delta E \sim \frac{2}{3}\frac{e^2}{c^3} w^2 t \sim \frac{2}{3}\frac{Z^2 e^6}{m^2 c^3 \rho^3 v}.$$

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*For larger accuracy we will preserve the numerical coefficient 2π. (A basic role in the expansion is played by "circular" frequencies, such that $\omega t \sim 1$.)

Effective radiation of frequency ν corresponds to electron emission with impact parameter from ρ to $\rho + d\rho$, connected with frequencies by the method shown above, so that

$$dq_\nu \sim \Delta E \cdot 2\pi\varrho\, d\varrho \sim \frac{4\pi}{3}\frac{Z^2e^6\, d\varrho}{m^2c^3\varrho^2 v} \sim \frac{8\pi^2}{3}\frac{Z^2e^6}{m^2c^3v^2}\, d\nu. \qquad (5.7)$$

Consecutive calculation of effective radiation by the formulas (5.6), (5.4) with g-vector, found from solution of mechanical problem about motion of electron along a hyperbolic orbit near an ion, is made in the book by L. D. Landau and Ye. M. Lifshits [1]. It gives:

$$dq_\nu = \frac{32\pi^2}{3\sqrt{3}}\frac{Z^2e^6}{m^2c^3v^2}\, d\nu \text{ when } \nu \gg \frac{mv^3}{2\pi Ze^2}, \qquad (5.8)$$

$$dq_\nu = \frac{32\pi}{3}\frac{Z^2e^6}{m^2c^3v^2} \ln\frac{mv^3}{1{,}78\pi\nu Ze^2}\, d\nu \text{ when } \nu \ll \frac{mv^3}{2\pi Ze^2}. \qquad (5{,}9)$$

As is evident, with large frequencies the exact result differs from a simple estimate (5.7) by only the numerical factor $4/\sqrt{3} = 2.3$. With small frequencies the exact formula differs from the simple estimate, besides by a numerical factor, also by a logarithmic factor depending on frequency. The fact is that small frequencies are radiated during far collisions with large impact parameters ρ, while when $\nu \to 0$, $\rho \to \infty$ collisions with parameters $\rho > \frac{v}{2\pi\nu}$ give relatively even greater and larger contribution in radiation of frequency ν as compared to collisions with parameters $\rho \sim \frac{v}{2\pi\nu}$, which are only considered at the conclusion of simple formula (5.7).

Divergence of effective radiation on the side of small frequencies is characteristic for a Coulomb field slowly dropping with distance, thanks to which distant collisions obtain so essential a role. This divergence is removed during calculation of shielding, always existing in a real gas. Actually with respect to ρ in formula (5.6) one should integrate not ad infinitum, but, let us say, to Debye radius d, which will limit radiation on the part of small frequencies to frequency

$\nu_{\min} \sim v/2\pi d$.

It is necessary, however, to note that integral radiation $q = \int dq_\nu$ along spectrum converges on the part of small frequencies, since dq_ν divergence is only logarithmic and contribution of peak dq_ν when $\nu \to 0$ in integral with respect to ν is small. Therefore, if one were interested in integral radiation, the question on impact parameters ρ from above, and frequencies — from below, is not so essential.

Radiation of large frequencies in the classical theory does not depend on frequency, and effective radiation on unit interval of frequencies $dq_\nu/d\nu$ remains final even when $\nu \to \infty$.* Formally, total radiation $q = \int dq_\nu$ diverges on the part of large frequencies.

This contradictory theory is connected with imperfection of classical presentations about motion of electron and is removed in the quantum theory. Large frequencies, as we have seen, are radiated during transit of electron past ion on small impact parameters. But according to quantum mechanical concepts, an electron possessing initial momentum $p = mv$ cannot be localized more exactly than is dictated by the indeterminancy principle $\Delta r \Delta_p \sim h/2\pi$. Inasmuch as uncertainty in momentum cannot exceed the actual momentum, there is no meaning in talk about impact parameters smaller than $\rho_{\min} \sim h/2\pi mv$. Maximum frequency radiated with such minimum impact parameters in order of magnitude, equals $\nu_{\min} \sim v/2\pi\rho_{\min} \sim mv^2/h$. This limitation of radiated frequency from above has a very graphic physical meaning. In the quantum theory bremsstrahlung is presented in the following way. A free electron, possessing initial energy $E = mv^2/2$, flying past an ion, can emit light quantum $h\nu$. If after emission of quantum it

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*This is accurate only under the condition that colliding particles possess opposite charges (electron — positive ion). During interaction of particles with charges of one sign $dq_\nu/d\nu \to 0$ when $\nu \to \infty$.

remains free, i.e., departing from the ion, it possesses positive energy E', then, obviously, the electron cannot emit quantum exceeding initial energy E. Thus, $\nu_{max} = \frac{E}{h} = \frac{mv^2}{2h}$, which with an accuracy of immaterial factor 1/2 coincides with limitation of frequency dictated by indeterminancy principle.

In quantum mechanics a free electron is presented as a plane wave and the idea of impact parameter does not have a strictly defined meaning. Is possible to speak about emission probability of quantum of one or another frequency, more correctly, about effective cross section of emission of quanta with energies from $h\nu$ to $h\nu + d\,(h\nu)$. The content of energy radiated in interval of frequencies $d\nu$ by a single electron stream interacting with one ion is equal to the product of energy of quantum $h\nu$ by effective cross section of emission $d\sigma_\nu$. This magnitude also corresponds to effective radiation of classical theory:

$$dq_\nu = h\nu \cdot d\sigma_\nu \text{ (erg}\cdot\text{cm}^2\text{)}. \tag{5.10}$$

In light of corresponding of principle the effective radiation of frequency ν is connected with transition of electron from one "stationary hyperbolic orbit," corresponding to energy of electron E, to another, corresponding to energy $E' = E - h\nu$. Effective cross section $d\sigma_\nu$, and consequently also effective radiation dq_ν are calculated in quantum mechanics by the usual methods, through matrix elements of energy of interaction of electron with ion.

However, before presenting the result of quantum-mechanical calculation of bremsstrahlung, we will see what are the limits of applicability of classical formulas (5.8), (5.9) and when, properly, it is necessary to replace them by quantum-mechanical formulas.

According to classical conclusion, formula (5.8) for large frequencies is accurate under the condition $\nu \gg mv^3/2\pi Ze^2$. Of course, there is no meaning in extending it to frequencies exceeding upper limit dictated by quantum energy concepts, $\nu_{max} = E/h = mv^2/2h$. Let us rewrite these limitations put on frequency in formula (5.8), in the form

$$1 = \frac{h\nu_{max}}{E} > \frac{h\nu}{E} \gg \frac{h}{E}\frac{mv^3}{2\pi Ze^2} = \frac{hv}{\pi Ze^2}. \tag{5.11}$$

But inequality $hv/\pi Ze^2 \ll 1$ with an accuracy of two constitutes nothing else but condition of quasiclassicality of motion of electron in a Coulomb field (see, for instance, [2])

$$\frac{hv}{2\pi Ze^2} \ll 1. \tag{5.12}$$

Therefore classical formula (5.8) for effective radiation of frequency ν, limited from above and from below by inequalities (5.11), may be approximately used in addition to all those velocities of electrons which satisfy inequality (5.12). If condition of quasiclassicality (5.12) holds, then domain of applicability of formula (5.8) spreads to very small frequencies, such that $h\nu/E \sim hv/\pi Ze^2 \ll 1$. Inasmuch as usually there is interest in quanta which are not very small as compared with kT, i.e., with energies of electrons, and contribution of peak when $\nu \rightarrow 0$ in integral radiation is small, formula (5.8) may be successfully extended to $\nu = 0$, replacing formula (5.9) and thereby removing formally divergence dq_ν when $\nu \rightarrow 0$.

Let us convert condition of quasiclassicality (5.12), which is condition of applicability of formula (5.8), thus, in order to obtain the condition put on energy of electron,

$$E = \frac{mv^2}{2} < \frac{m}{2}\left(\frac{2\pi Ze^2}{h}\right)^2 = \frac{Z^2e^2}{2a_0} = I_H Z^2 = 13{,}5Z^2 \text{ ev}, \tag{5.13}$$

where $a_0 = h^2/4\pi^2me^2$ is Bohr radius, and $I_H = 13.5$ ev is the potential ionization of an atom of hydrogen.*

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*Condition of quasiclassicality for motion of electron in Coulomb field is equivalent to condition of smallness of energy of electron as compared to its energy on first Bohr orbit.

For instance, in the case of hydrogen plasma formula (5.8) is accurate up to temperatures of the order of 10 ev ~ 100,000°K; in gas from heavier elements it is accurate to still higher temperatures, since due to multiple ionization charges of Z ions increase. Thus, in air of normal density at $T = 10^6$ °K $Z \approx 6$ and average energy of electrons is four times less than the "quasiclassical" limit.

At very high temperatures, when there are inequalities opposite to the conditions of quasiclassicality (5.12), (5.13), the Born approximation in quantum mechanics* is accurate. For unrelativistic energies ($E \ll mc^2$ = 500 kev calculation of effective radiation in Born approximation gives the expression (see [3]):

$$dq_\nu = h\nu \cdot d\sigma_\nu = \frac{32\pi}{3}\frac{Z^2e^6}{m^2c^3v^2}\ln\frac{(\sqrt{E}+\sqrt{E-h\nu})^2}{h\nu}\,d\nu,$$

dq_ν automatically turns into zero when $h\nu = E$ and weakly, logarithmically, depends on frequency in whole interval of frequencies from 0 to ν_{max}.

It is remarkable that the quantum formula leads to values of effective radiation very close to those given by the classical formula (5.8) (with the exception, of course, of frequencies very small and very close to maximum). This may be seen from Table 5.1, in which are presented values of the ratio

$$\varphi = \left(\frac{dq_\nu}{d\nu}\right)_{\text{квант}} \Big/ \left(\frac{dq_\nu}{d\nu}\right)_{\text{класс}} = \frac{\sqrt{3}}{\pi}\ln\frac{(1+\sqrt{1-x})^2}{x}$$

depending upon dimensionless value $x = \frac{h\nu}{E} = \frac{\nu}{\nu_{max}}$.

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*For Born approximation it is necessary that not only at initial, but also at terminal velocity of electron conditions (5.12), (5.13) hold; otherwise one should use exact wave functions of electron in Coulomb field, which introduces known Coulomb factor into resultant formulas [2, 3].

Table 5.1.

x	0	0,1	0,2	0,3	0,4	0,5	0,6	0,7	0,8	0,9	1
φ	∞	2,01	1,61	1,34	1,13	0,97	0,81	0,68	0,53	0,36	0

Integral radiation, calculated by quantum formula, is written in the following form:

$$q_{\text{квант}} = \int_0^{\nu_{\max}} \left(\frac{dq_\nu}{d\nu}\right)_{\text{квант}} d\nu = \left(\frac{dq_\nu}{d\nu}\right)_{\text{класс}} \nu_{\max} \int_0^1 \varphi\, dx = 1{,}05\ q_{\text{класс}}.$$

Thus, it is possible to use classical formula (5.8) with good approximation for practically any non-relativistic temperatures.

§ 3. Free-Free Transitions in Heated Gas

Let us find radiating ability of ionized gas, connected with bremsstrahlung.

Let us assume that in 1 cm^3 gas there are N_+ positive ions with charge Ze and N_e electrons with Maxwellian distribution with respect to velocities $f(v')dv'$ $(\int_0^\infty f(v')dv' = 1)$. The temperature of the electron gas will be designated by T. Energy which is radiated by electrons possessing velocities from v' to $v' + dv'$, in 1 cm^3 in 1 sec for the interval of frequencies from ν to $\nu + d\nu$ is equal to

$$N_+ N_e f(v')\, dv' v'\, dq_\nu\ .^* \tag{5.14}$$

The content of energy spontaneously radiated as a result of free-free transitions in interval $d\nu$ in 1 cm^3 for 1 sec will be obtained, if one integrates expression (5.14) with respect to velocities of electrons from v_{min} to ∞, where v_{min} is minimum velocity of electrons able to radiate quantum $h\nu$: $\frac{mv^2_{min}}{2} = h\nu$. Using formula (5.8) for effective radiation and integrating, we will find spectral radiating ability connected with the deceleration mechanism:

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*Is assumed that velocities of ions are very small as compared to velocities of electrons.

$$J_\nu d\nu = \frac{32\pi}{3}\left(\frac{2\pi}{3kTm}\right)^{\frac{1}{2}}\frac{Z^2e^6}{mc^3}N_+N_e e^{-\frac{h\nu}{kT}}d\nu. \tag{5.15}$$

Emission of large quanta $h\nu \gg kT$ is exponentially small. This is connected with the fact that large quanta are radiated by electrons with high energies, concentrated in tail of Maxwellian distribution with respect to velocities.

Integral radiating ability for bremsstrahlung is equal to

$$J = \int_0^\infty J_\nu d\nu = \frac{32\pi}{3}\left(\frac{2\pi kT}{3m}\right)^{\frac{1}{2}}\frac{Z^2e^6}{mc^3h}N_+N_e =$$

$$= 1{,}42\cdot 10^{-27}Z^2T^{\circ\frac{1}{2}}N_+N_e \text{ erg/cm}^3\text{sec} \tag{5.16}$$

(T° – temperature in Kelvin degrees).

Integral deceleration emission rather weakly depends on temperature (it is proportional to $\sqrt{T}$).

If in the gas are ions of various Z charges, then formulas (5.15), (5.16) should be summed over all sorts of ions.

Now we will find coefficient of deceleration absorption of light. For this we will use principle of detailed balancing. If $U_{\nu p}$ is equilibrium spectral density of radiation, determined by formula of Planck (2.10),

$$U_{\nu p} = \frac{8\pi h\nu^3}{c^3}\frac{1}{e^{\frac{h\nu}{kT}}-1}, \tag{5.17}$$

and a_ν is the spectral coefficient of true deceleration absorption, calculated on one ion and one electron moving with velocity v, then the quantity of radiation in the interval of frequencies from ν to $\nu + d\nu$, absorbed during thermodynamic equilibrium in 1 sec for 1 cm^3 by electrons with velocities from v to v + dv, equals

$$N_+N_eU_{\nu p}d\nu\cdot cf(v)dv\cdot a_\nu\left(1-e^{-\frac{h\nu}{kT}}\right). \tag{5.18}$$

Factor $(1 - e^{-\frac{h\nu}{kT}})$ considers effective decrease of absorption owing to forced emission (over-radiation; see § 4 Ch. II). In conditions of thermodynamic equilibrium absorption and emission accurately compensate one another, i.e., expressions (5.18) and (5.14) are equal. Velocities of electrons emitting quantum $h\nu$ and absorbing these quanta, are connected by the law of conservation of energy

$$\frac{mv'^2}{2} = \frac{mv^2}{2} + h\nu. \tag{5.19}$$

Noticing that $v\,dv = v'\,dv'$ and using formula (5.8) for dq_ν we will find from equalities (5.14) and (5.18):

$$a_\nu = \frac{4\pi}{\sqrt{3}} \frac{Z^2 e^6}{hcm^2 v \nu^3}. \tag{5.20}$$

This formula was obtained by Kramers in 1923. Multiplying a_ν by $N_+ N_e$ and, using Maxwellian distribution function, averaging with respect to velocities of electrons, we will obtain spectral coefficient of true deceleration absorption in gas at a temperature of electrons T:

$$\varkappa_\nu = \frac{4}{3}\left(\frac{2\pi}{3mkT}\right)^{\frac{1}{2}} \frac{Z^2 e^6}{hcm\nu^3} N_+ N_e = 3{,}69\cdot 10^8 \frac{Z^2}{T^{\circ\frac{1}{2}}\nu^3} N_+ N_e\, \text{см}^{-1}$$
$$= 4{,}1\cdot 10^{-23} Z^2 \frac{N_+ N_e}{T^{\circ\frac{7}{2}} x^3}\, \text{см}^{-1}, \quad x = \frac{h\nu}{kT}. \tag{5.21}$$

Remembering determination of average coefficient of absorption, characterizing radiating ability (2.102), we will calculate this magnitude for deceleration mechanism:

$$\varkappa_1 = \frac{J}{cU_p} = \frac{J}{4\sigma T^4} = 6{,}52\cdot 10^{-24} Z^2 \frac{N_+ N_e}{T^{\circ\frac{7}{2}}}\, \text{см}^{-1}. \tag{5.22}$$

Corresponding average range is equal to

$$l_1 = \frac{1}{\varkappa_1} = 1{,}53\cdot 10^{23} \frac{T^{\circ\frac{7}{2}}}{Z^2 N_+ N_e}\, \text{см}. \tag{5.23}$$

Let us calculate average Rosseland path (2.80) for the case when gas is completely ionized and deceleration mechanism of absorption is unique (and all ions possess identical Z charge)

$$l = 4{,}8\cdot 10^{24}\frac{T^{\circ\frac{7}{2}}}{Z^3 N_+ N_e}\,\text{см.} \tag{5.24}$$

Rosseland path l for deceleration mechanism is equal to spectral run with energy of quanta $h\nu = 5.8kT$. As can be seen, in transfer of radiant energy by means of thermal conduction with deceleration mechanism of absorption a basic role is played by very large quanta found in the Wien region of the spectrum. Conversely, during volume radiation a basic role is played by small quanta. Average coefficient $\varkappa_1$ is equal to spectral coefficient $\varkappa_1$ $(1 - e^{-h\nu/kT})$, corrected on forced emission, corresponding to $h\nu = 1.73kT$.

In order to imagine the order of magnitudes of optical characteristics of plasma, corresponding to deceleration mechanism, we will give a specific example.

Let us consider hydrogen at density $\rho = 1.17\cdot 10^{-6}$ g/cm^3 (such density corresponds to a pressure of 10 mm Hg at room temperature) and temperature $T = 100{,}000^\circ$K. In these conditions hydrogen is completely dissociated and is completely ionized, so that $N_+ = N_e = 7\cdot 10^{17}$ cm^{-3}.

The coefficient of absorption of red light $\lambda = 6500$ A here equals $\varkappa_\nu = 5.7\cdot 10^{-3}$ cm^{-1}, and range $l_\nu = 1/\varkappa_\nu = 175$ cm.

The Rosseland path $l = 3.1\cdot 10^6$ cm. The mean path characterizing radiating ability, $l_1 = 0.98\cdot 10^5$ cm.

If dimensions of body are much less than length l_1, then the body emits as a volume radiator (see § 16 Ch II) and speed losses of energy on radiation equal

$$\frac{d(\rho\varepsilon)}{dt} = -J,$$

where ε is specific internal energy. In our example $J = 2.2\cdot 10^{11}$ erg/cm^3 sec. Taking into account energy of dissociation and ionization

ε = 41.6 ev/atom, $\rho\varepsilon = 4.66 \cdot 10^7$ erg/cm^3. Initial scale of time of radiant cooling $\tau = \rho\varepsilon/J = 2.12 \cdot 10^{-4}$ sec

§ 4. Effective Capture Cross Section of an Electron by an Ion with Emission of Quantum

Let us consider the capture of a free electron by a hydrogen-like "ion" with quantum emission and formation of a hydrogen-like "atom." We will, as in § 2, originate from semiclassical presentations. In classical mechanics without taking into account radiation the transition from free states of an electron to bound states is continuous. The state or orbit of an electron are characterized by magnitude of total energy of electron — ion system E and (in general) instead of "impact distance" ρ is angular momentum, also determining geometric parameters of trajectory. With decrease of energy and constant moment the hyperbolic orbits, corresponding to positive energy $E > 0$, continuously change to parabolic orbits ($E = 0$) and further, in a bound state of the system, characterized by negative energy, $E < 0$, into elliptic orbits (Fig. 5.3). In light of correspondence principle the capture of a free electron and quantum emission, whose energy exceeds initial kinetic energy of electron E, are connected with transition of electron from a hyperbolic trajectory to an elliptic trajectory.

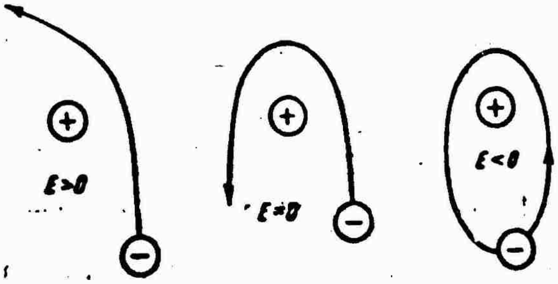

Fig. 5.3. Hyperbolic, parabolic, and elliptic orbit of electron.

In classical mechanics energy of an electron — ion system can be arbitrary. In quantum mechanics the energy spectrum of a system is continuous only if the electron is free and $E > 0$. In the bound state, when $E < 0$, energy can take only discrete values. Energy levels of hydrogen-like atom E_n are characterized by the prime quantum number n, going through values from 1 to ∞,

$$E_n = -\frac{I_H Z^2}{n^2} = -\frac{I}{n^2}, \quad I_H = \frac{e^2}{2a_0} = \frac{2\pi^2 m e^4}{h^2}. \tag{5.25}$$

$I = I_H Z^2 = |E_1|$ is the absolute value of energy of the ground state, i.e., ionization potential. Binding energy of electron in n-th quantum state equals $-E_n = |E_n| = I/n^2$. A diagram of levels of an atom of hydrogen is depicted in Fig. 2.2 in § 2 Ch. II. As is known, during motion of a bound electron in a Coulomb field of an ion its kinetic energy on the average with respect to time is equal to half of the potential taken with the opposite sign, and is equal to the total, also taken with reverse sign: $E_{kin} = -E_{pot}/2 = -E (E = E_{kin} + E_{pot})$. Consequently, on the average with respect to time

$$E_{\text{кин}} = \frac{m\bar{v}^2}{2} = \frac{I}{n^2} = \frac{I_H Z^2}{n^2}.$$

From this formula, taking into account inequality (5.13) it is clear that motion of an electron in strongly excited quantum states with large quantum number n is quasiclassic.

In examining bremsstrahlung,in § 2 we applied classical formula (5.8) for effective radiation, describing by it "transitions" of an electron from one hyperbolic orbit to another, corresponding to less energy, while they extended the formula up to transitions to an orbit with infinitely small positive energy, almost parabolic, which corresponded to radiation of maximum frequency $\nu_{max} = E/h$. Here, of course, initial energy E was assumed sufficiently small, $E \ll I_H Z^2$, $v \ll 2\pi Z e^2/h$, so that motion in initial state was quasiclassic. Motion in final state is all the more quasiclassic, since an electron during transition loses kinetic energy and decelerates. Inasmuch as small negative energies, as we just now saw, also correspond to small velocities and corresponding elliptic orbits are also close to parabolic (but only on the part of negative energies), it is natural to extend formula (5.8) also to the case of radiation of frequencies somewhat in excess of ν_{max}, i.e., to the case of capture of an electron on high levels. One should consider here that the final state of an electron falls in the discrete spectrum. Effective radiation in certain small, but finite interval of frequencies $\Delta\nu$, $\Delta q_\nu = (dq_\nu/d\nu)\Delta\nu$, is equal according to quantum treatment to $h\nu\Delta\sigma_\nu$, where $\Delta\sigma_\nu$ is effective cross-section for emission of quanta in small interval $\Delta\nu$. But now emission of quanta from $h\nu$ to $h\nu + \Delta(h\nu)$ corresponds to capture on a defined finite number of levels Δn and effective capture cross section of them $\Delta\sigma_\nu$ can be presented in the form of product $\sigma_{cn}\Delta n$ where σ_{cn} is the mean cross section of capture on any of the levels in this interval. This cross section depends on average number n in small interval Δn. Thus,

$$\sigma_{cn}=\frac{\Delta\sigma_\nu}{\Delta n}=\frac{1}{h\nu}\frac{\Delta q_\nu}{\Delta n}=\frac{1}{h\nu}\left(\frac{dq_\nu}{d\nu}\right)\frac{\Delta\nu}{\Delta n}. \tag{5.26}$$

Using formula (5.25) for determination of energy distance between levels for large n: $\left|\frac{dE_n}{dn}\right| = \frac{h\Delta\nu}{\Delta n} = 2I_H Z^2/n^3$ and formula (5.8) for effective radiation, we will obtain effective capture cross section on level n of a free electron possessing initial energy $E = mv^2/2$:

$$\sigma_{cn}=\frac{128\pi^4}{3\sqrt{3}}\frac{Z^4e^{10}}{mc^3h^6v^2\nu}\cdot\frac{1}{n^3}=\frac{2{,}1\cdot10^{-22}}{n^3}\frac{I_H Z^2}{E}\frac{I_H Z^2}{h\nu}\,\text{cm}^2. \tag{5.27}$$

Energy of quantum emitted during capture of electron on level n equals

$$h\nu=E+|E_n|=\frac{mv^2}{2}+\frac{I_H Z^2}{n^2}. \tag{5.28}$$

As quantum-mechanical calculations show (see following paragraph), semiclassical formula (5.27) gives good results also in reference to capture on deep levels, including also on ground levels (n = 1), in spite of the fact that motion of electron in the ground state is no longer quasiclassic ($E_{kin} = \frac{m\overline{v}^2}{2} = I_H Z^2$).*

Let us calculate with the help of formula (5.27) the total effective cross section of photocapture of electron with given energy $E = mv^2/2$ on all levels of hydrogen-like ion. For this one should sum cross section σ_{cn} over the formula (5.27) for all n from 1 to ∞ taking into account the fact that quanta of different energies are emitted, which are given by formula (5.28):

$$\sigma_c = 2{,}1\cdot 10^{-22}\,\frac{I_H Z^2}{E}\sum_{n=1}^{\infty}\frac{1}{n^3}\,\frac{1}{\left(\frac{E}{I_H Z^2}+\frac{1}{n^2}\right)} = \frac{2{,}8\cdot 10^{-21} Z^2}{E_{эв}}\,\varphi\left(\frac{I_H Z^2}{E}\right). \qquad (5.29)$$

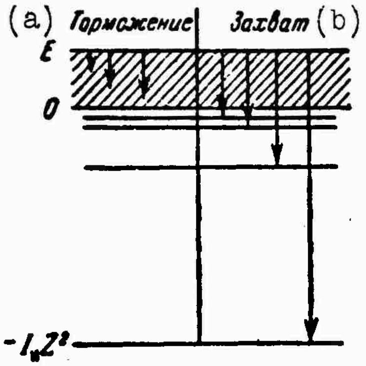

Fig. 5.4. Diagram explaining relationship between energy intervals of final states of electron during deceleration and capture by ion. KEY: (a) deceleration, (b) capture.

Here φ designates sum over n. In rough approximation for small energies of electrons $E \ll I_H Z^2$, $\varphi \approx \left(\sum_{n=1}^{n^*}\frac{1}{n}\right)+\frac{1}{2}$, where $n^* \approx (I_H Z^2/E)^{1/2}$. For small (but also not very small) energies of electrons, when E is less than $I_H Z^2$, but comparable with this magnitude, the sum of φ is of the order 1 and capture cross section equals approximately $\sigma_c \approx 3\cdot 10^{-21}\,\frac{Z^2}{E_{ev}}$ cm^2.

It is interesting to compare integral effective radiation of free electron with given energy E during deceleration in field of hydrogen-like ion with integral radiation during photocapture, i.e., magnitudes $q_{dec} = \int dq_\nu = \int h\nu\, d\sigma_{dec}$ and $q_{cap} = \sum_n h\nu\sigma_{cn}$. The first magnitude according to (5.8) equals $q_{dec} = (dq_\nu/d\nu)\, E/h$, and the second, in virtue of the actual derivation of cross section σ_{cn} (see formula (5.26)), $q_{cap} = \left(\frac{dq_\nu}{d\nu}\right) \times \frac{I_H Z^2}{h}$, where constant $(dq_\nu/d\nu)$, is determined by formula (5.8). Both magnitudes, q_{dec} and q_{cap}, are proportional to energy intervals of possible final

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*Initial motion of free electron is assumed to be quasiclassical, i.e., initial energy $E \ll I_H Z^2$.

states of electron (Fig. 5.4) and relate to one another as these intervals:

$$\bar{q}_{\max}/q_{\text{непр}} = I_H Z^2/E.$$

§ 5. Effective Cross Section of Bound-Free Absorption of Light by Atoms and Ions

Let us consider the process which is opposite to that of photo-capture — photo-ionization of a hydrogen-like atom, i.e., absorption of quantum with transition of electron into continuous spectrum.

As in calculation of deceleration absorption, we will use principle of detailed balancing.

In 1 cm^3 in 1 sec there are

$$N_+ N_e f(v)\,dv\cdot v\cdot\sigma_{cn} \tag{5.30}$$

acts of photo-capture of electrons with velocities from v to v + dv on n-th level of ions. Quanta are emitted with frequencies from ν to $\nu + d\nu$, which are connected with velocity of an electron by relationship (5.28).

The number of reverse processes: acts of photo-ionization of "atoms" remaining in n-th quantum state, by quanta with frequencies from ν to $\nu + d\nu$, equals

$$N_n \frac{U_{\nu p}}{h\nu}\,d\nu\cdot c\cdot\sigma_{\nu n}\left(1-e^{-\frac{h\nu}{kT}}\right), \tag{5.31}$$

where $\sigma_{\nu n}$ is the effective absorption cross section of quantum $h\nu$ by an atom in the n-th state, N_n is the number of such atoms in 1 cm^3; factor $(1 - e^{-h\nu/kT})$, as earlier, considers forced emission. In conditions of total thermodynamic equilibrium f(v) is function of Maxwellian distribution of electrons, $U_{\nu p}$ is Planck function; the number of excited atoms N_n is expressed by Boltzmann formula:

$$N_n = N_1 \frac{g_n}{g_1} e^{-\frac{(E_n-E_1)}{kT}} = N_1 \frac{g_n}{g_1} e^{-\frac{I}{kT}\left(1-\frac{1}{n^2}\right)}, \tag{5.32}$$

where $g_n = 2n^2$ is static weight of n-th level of hydrogen-like atom, and N_1 is the number of atoms in 1 cm^3 remaining in the ground state; $g_1 = 2$; $E_n - E_1 = I_H Z^2 \left(1 - \frac{1}{n^2}\right) = I \left(1 - \frac{1}{n^2}\right)$ is the excitation energy of the n-th state.

The numbers of free electrons, ions, and "neutral" atoms (if $Z > 1$, then "neutral" hydrogen-like atom is an ion with charge $Z - 1$) are connected by the equation of Saha (see formula (3.44) in § 5 Ch. III):

$$\frac{N_+ N_e}{N} = 2\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}} \frac{u_+}{u} e^{-\frac{I}{kT}}, \tag{5.33}$$

while in this case the electron statistical sum of an ion $u_+ = 1$. The number of "neutral" atoms in 1 cm^3 $N = uN_1/g_1$, where u is the electron statistical sum of an atom.

Equating the numbers of direct and reverse processes to each other (5.30), (5.31) taking into account all remarks on magnitudes in the formulas, we will find effective absorption cross section of quantum $h\nu$ by a hydrogen-like atom, the charge of the "atomic" remainder of which equals Z and which is in the n-th quantum state:

$$\sigma_{\nu n} = \frac{64\pi^4}{3\sqrt{3}} \frac{e^{10} m Z^4}{h^6 c \nu^3 n^5} = 7{,}9 \cdot 10^{-18} \frac{n}{Z^2} \left(\frac{\nu_n}{\nu}\right)^3 \text{см}^2. \tag{5.34}$$

Here through ν_n designates minimum frequency of quantum, which is able to pull electron from n-th level: $h\nu_n = I_H Z^2/n^2$, (see formula (5.28)).

A characteristic peculiarity of the cross section is the inverse cubic dependence on frequency $\sigma_{\nu n} \sim (\nu_n/\nu)^3$. The cross section is maximum for threshold of absorption when $\nu = \nu_n$. Formula (5.34) is known in literature under the name of the Kramer formula.

Somewhat more strict, quantum-mechanical consideration of photoionization of hydrogen-like atoms from high levels leads to a formula differing from (5.34) by correction factor [4]:

$$g' = 1 - 0{,}173\left(\frac{h\nu}{I_H Z^2}\right)^{\frac{1}{3}}\left[\frac{2}{n^3}\left(\frac{I_H Z^2}{h\nu}\right) - 1\right].$$

In the majority of cases having a practical interest this factor is very close to unity, so that it, as a rule, cannot be considered.

Semiclassical formula (5.34), by its very own derivation is accurate only for highly excited states of n >> 1; nonetheless it gives good results even when it is applied to photo-ionization from ground level n = 1.

Quantum-mechanical calculations of effective cross section of photoeffect with K-shell of atoms, i.e., for ground state of hydrogen-like atom, carried out with exact wave functions of free electron, in a Coulomb field give [5] (from calculation on one electron, as also (5.33)):

$$\sigma_{\nu_1} \approx \frac{6{,}34\cdot 10^{-18}}{Z^2}\left(\frac{\nu_1}{\nu}\right)^{\frac{8}{3}}, \quad \nu - \nu_1 \ll \nu_1; \tag{5.35}$$

$$\sigma_{\nu_1} \approx \frac{8{,}32\cdot 10^{-18}}{Z^2}\left(\frac{\nu_1}{\nu}\right)^{3}, \quad \nu - \nu_1 \sim \nu_1; \tag{5.36}$$

$$\sigma_{\nu_1} \approx \frac{5{,}42\cdot 10^{-17}}{Z^2}\left(\frac{\nu_1}{\nu}\right)^{3,5}, \quad \nu \gg \nu_1. \tag{5.37}$$

The first of the formulas corresponds to region near boundary of absorption, the last one — when energy of liberated electron is considerably larger than binding energy $h\nu_1 = I_H Z^2$, which corresponds to transition to Born approximation.

Comparison of formula (5.34), in which we will put n = 1, with formulas (5.35), (5.36) shows that on boundary of absorption, when $\nu = \nu_1$, "semiclassical cross section" (5.34) equals $7.9\cdot 10^{-18}/Z^2$ cm^2 and in all is 25% larger than quantum (5.35). When $\nu - \nu_1 \sim \nu_1$, i.e., when energy of liberated electron is of the order of the binding energy of it in the ground state of the atom, formulas (5.34), (5.35) coincide with 5% accuracy and even give identical dependence on frequency. There is strong deviation only when $h\nu \gg I_H Z^2$, when energy of liberated electron $E \gg I_H Z^2$, i.e., in Born region, where position is opposite to quasi-classical.

As will be seen further, such large quanta always are in far Wien region of spectrum and under conditions close to thermal equilibrium, do not play a practical role. Thus, semiclassical formula (5.34) may be approximately extended to photo-ionization from all levels of hydrogen-like atoms. Exactly so, the formula for photo-capture (5.27) is applicable for capture of electron on all levels up to ground level, as was used in the preceding section during calculation of total capture cross section.

Let us consider briefly what it is possible to expect from application of formulas derived for hydrogen-like atoms to complex atomic systems.

Small quanta, considerably smaller than ionization potential I of atom or ion, are absorbed (knocking out an electron) only by highly excited atoms (ions) whose excitation energy is not less than $I - h\nu$. But in strongly excited states the optical electron moves along a great orbit, in whose region the field of "atomic remainder" is very close to a Coulomb field, created by a charge equal to the charge of the "remainder." Therefore, it is possible to trust that in this case approximation of "hydrogen similarity" is justified. Unfortunately, there are no exact quantum-mechanical calculations of absorption by highly excited atoms and ions, which could confirm this rather probable assumption.

The available calculations, which are not numerous, pertain mainly to photoeffect from ground state of atoms (for ions, data are even less).

In this case the field in which absorbing electron moves is created by a complex system of charges of the nucleus and remaining electrons, the dimensions of which are the same as the "orbit" of the electron, and, of course, the field strongly differs from a Coulomb field. Exactly so, the wave function of an electron strongly differs from the wave function of the S-state of a hydrogen-like atom. For a number of atoms effective cross sections of photo-ionization from the ground state very strongly differ from corresponding cross section for an atom of hydrogen, equal according to (5.34) to $\sigma_{\nu 1} = 7.9 \cdot 10^{-18}$ $(\nu_1/\nu)^3$ cm^2 (on boundary of absorption $\sigma^* = 7.9 \cdot 10^{-18}$ cm^2), for others they are very close on boundary of absorption, but have another dependence on frequency. Thus, for instance, for oxygen and fluorine on boundary of absorption the cross sections are equal approximately $2.5 \cdot 10^{-18}$ cm^2, and then hardly depend on frequency up to $\nu \approx 2\nu_1$. For nitrogen on boundary $\sigma^* = 7.5 \cdot 10^{-18}$ cm^2, and for carbon $\sigma^* = 10 \cdot 10^{-18}$ cm^2, but the cross sections drop with increase of ν slower than $\sim\nu^{-3}$, as for hydrogen-like atoms; for lithium $\sigma^* = 3.7 \cdot 10^{-18}$, for calcium $\sigma^* = 25 \cdot 10^{-18}$ cm^2. Especially great is the distinction from "hydrogen-likeness" for alkali metals. For sodium $\sigma^* = 0.31 \cdot 10^{-18}$ cm^2.

Experimental values for rubidium $\sigma^* = 0.1 \cdot 10^{-18}$ cm^2, for cesium $\sigma^* = 0.6 \cdot 10^{-18}$ cm^2. A more detailed survey of available data can be found in an article by Beyts [7]. Fortunately, as we will see below, in sufficiently rarefied gases in states which are close to thermodynamic equilibrium, the role of large quanta, exceeding ionization potentials of atoms and ions, is comparatively small, so that strong divergences in this case do not make senseless use of approximation of "hydrogen-similarity."

In certain cases there is a large value in photo-capture of

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*Graphs for cross sections of photo-ionization from ground state of O, N, F, C are given in [6].

electrons by neutral atoms with formation of negative ions and, correspondingly, photoelectric absorption of quanta by negative ions. This pertains to negative ions of hydrogen, playing the most important role in absorption of light in stellar atmospheres, and negative ions of oxygen, essential for absorption of light in air in certain conditions. Binding energies of ionization potentials of negative ions, determining lower bound of absorption $h\nu_{min}$, equal 0.75 ev for hydrogen, 1.45 ev for atomic ions of oxygen O^- of the order of several tenth ev for molecular ions O_2^-. Dependence of cross section on frequency has nothing in common with the law that ν^{-3}. In Fig. 5.5 are presented results of quantum-mechanical calculations of effective cross section of photo-ionization of O^-. The graph is taken from [8]. Around theoretically calculated curve are shown experimental points according to measurements [9]. Data on absorption by H^- ions can be found in [6].

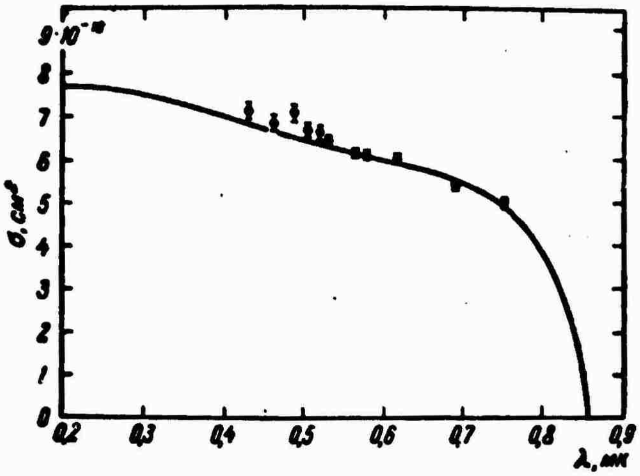

Fig. 5.5. Effective absorption cross section of light by negative O^- ions of oxygen.

§ 6. Coefficient of Continuous Absorption in Gas from Hydrogen-Like Atoms

Let us calculate coefficient of bound-free absorption of $h\nu$ quanta by hydrogen-like atoms, whose "nucleus" charge equals Z. At a given

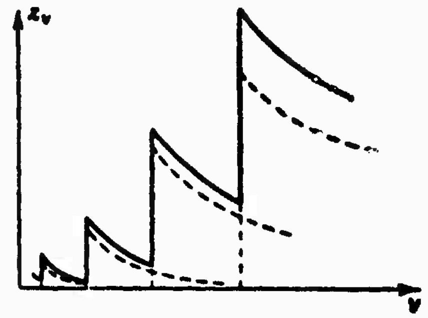

Fig. 5.6. "Paling" of absorption. Dotted curves correspond to absorption by atoms in given quantum state. Solid curve is total coefficient of absorption. The figure is schematic.

For large n, when index in exponent does not depend practically on n, the number of atoms N_n is simply proportional to n^2 ($g_n = 2n^2$).

Inasmuch as effective cross section $\sigma_{\nu n} \sim n^{-5}$, components in sum (5.38) when $n \rightarrow \infty$ decrease in proportion to $1/n^3$, so that contribution in absorption of light of a given frequency of all the higher and higher levels very rapidly decreases, and actual infinite sum converges.*

We will be interested by temperatures at which degree of ionization is small. As was shown in § 5 Ch. III, noticeable ionization in not too dense a gas starts when kT is still much less than ionization potential I. The number of excited atoms here is minute, since for excitation even the lowest state n = 2 energy close to ionization potential and equal to 3/4 I is necessary.

Thus, when kT << I the number of atoms in the ground state N_1 is very close to full number of atoms $N = \Sigma N_n$ and in formula of Boltzmann (5.32) it is possible to set approximately $N_1 \approx N$. Under this condition setting N_n and $\sigma_{\nu n}$ by the formulas of (5.32), (5.34) in expression (5.38) and introducing designations:

$$\left.\begin{aligned} x_n &= \frac{|E_n|}{kT} = \frac{|E_1|}{kT} \cdot \frac{1}{n^2} = \frac{x_1}{n^2}, \\ x_1 &= \frac{|E_1|}{kT} = \frac{I_H Z^2}{kT} = \frac{I}{kT}, \\ x &= \frac{h\nu}{kT}, \end{aligned}\right\} \qquad (5.39)$$

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*In real gas due to interaction of atoms and ions upper levels will be cutaway (see § 6 Ch. III), so that in fact the number of members in sum (5.38) is finite. In this case there is no necessity to cut the sum with respect to n since the sum converges rapidly.

We will obtain coefficient of bound-free absorption in the form

$$\varkappa_\nu' = \frac{64\pi^4}{3\sqrt{3}} \frac{e^{10} m}{k} \frac{Z^4 N}{\nu^3} \sum_{n^*}^{\infty} \frac{1}{n^3} e^{-(x_1 - x_n)}. \tag{5.40}$$

In order to obtain full coefficient of continuous absorption, to $\varkappa_\nu'$ one should join coefficient of deceleration absorption by free electrons in field of ionized atoms — "hydrogen-like ions" — which is given by formula (5.21). Expressing in this formula the product N_+N_e by the number of "neutral" atoms according to the formula of Saha (5.33) and considering that $u \approx g_1 = 2$, $N \approx N_1$, we will rewrite the coefficient of deceleration absorption in the form

$$\varkappa_\nu'' = \frac{16\pi^2}{3\sqrt{3}} \frac{Z^2 e^6 kTN}{h^4 c \nu^3} e^{-\frac{I}{kT}} = \frac{64\pi^4}{3\sqrt{3}} \frac{Z^4 e^{10} m N}{h^6 c \nu^3} \frac{e^{-x_1}}{2x_1}. \tag{5.41}$$

Total coefficient $\varkappa_\nu = \varkappa_\nu' + \varkappa_\nu''$ equals

$$\varkappa_\nu = \frac{64\pi^4}{3\sqrt{3}} \frac{e^{10} m Z^4 N}{h^6 c \nu^3} \left\{ \sum_{n^*}^{\infty} \frac{1}{n^3} e^{-(x_1 - x_n)} + \frac{e^{-x_1}}{2x_1} \right\}. \tag{5.42}$$

This formula is considerably simplified if energy of quantum is small as compared to ionization potential, so that quantum is absorbed only by highly excited atoms (n* is great). Inasmuch as levels rapidly condense with growth of n, summation with a large n can be replaced by integration ("differential" corresponds to $\Delta n = 1$). Integration with respect to n is equivalent to integration with respect to spectrum of energy states with replacement of discrete spectrum by continuous, in accordance with equality $dn/n^3 = -1/2\ dx_n/x_1$.

As the lower limit of the integral with respect to x_n, one should, obviously, take dimensionless energy of quantum $x = h\nu/kT$. Thus,

$$\sum_{n^*}^{\infty} \frac{1}{n^3} e^{-(x_1 - x_n)} \approx -\frac{e^{-x_1}}{2x_1} \int_x^0 e^{x_n} dx_n = \frac{e^{-x_1}}{2x_1} (e^x - 1). \tag{5.43}$$

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*It is frequently called the Kramer — Unsöld formula.

If one were to formally extend summation or integration to "negative binding energies" or, which is the same, to energy of "excitation" $x_1 - x_n$, exceeding ionization potential, then the integral with respect to x_n from 0 to $-\infty$ yields magnitude $e^{-x_1}/2x_1$, accurate to corresponding free-free transitions. This should have been expected, since the states of an atom with "excitation" exceeding the ionization potential are states with a detached electron, and continuous transition from bound state of electron to free state was from the very beginning assumed on the basis of derivation of effective cross section of bound-free absorption.

Putting expression (5.43) in formula (5.42), removing in the coefficient standing before the brackets, factor $I/kT = I_H Z^2/kT$ and reducing it by magnitude x_1, contained in denominator of (5.43), we will obtain final formula for coefficient of absorption of small quanta $h\nu \ll I$:*

$$\varkappa_\nu = \frac{16\pi^2}{3\sqrt{3}} \frac{e^6 Z^2 kTN}{h^4 c \nu^3} e^{-\frac{I-h\nu}{kT}} = 0{,}96\cdot 10^{-7} \frac{NZ^2}{T^{\circ 2}} \frac{e^{-(x_1-x)}}{x^3} \text{см}^{-1}. \qquad (5.44)$$

Coefficient of absorption $\varkappa_\nu$ is proportional not to Z^4, as it can appear by looking at formula (5.40), but only to Z^2. In order to explain this, we will remember, what the origin is of factor Z^4 in formula (5.40). One factor Z^2 enters into the coefficient in connection with proportionality of effective absorption cross section to the square of "acceleration" of electron in Coulomb field (according to classical treatment) or square of matrix element of energy of interaction with "nucleus" (according to quantum treatment). The other factor Z^2 appeared due to proportionality of absorption cross section $\sigma_{\nu n}$ to the distance between levels, which in turn is proportional to total energy interval of bound states, $I = I_H Z^2$.

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*It is frequently called the Kramer — Insöld formula.

Cross section $\sigma_{\nu n}$, indeed, is proportional to the energy distance between levels, since the cross section of photo-capture is proportional to this distance (see formula (5.21)), which is connected with absorption cross section by the principle of detailed balancing. During summation of partial coefficient $\varkappa'_{\nu n} = N_n \sigma_{\nu n}$ over levels or, which is the same, during integration with respect to energy interval of bound states participating in absorption of given quantum, the last dependence on Z^2 disappears. The remark on dependence of $\varkappa_\nu$ on Z is essential for transition to multiply charged ions (see below).

As can be seen from formulas (5.42), (5.43), bound-free transitions and free-free transitions introduce into total coefficient of continuous absorption $\varkappa_\nu$ fractions, which are related to one another as

$$(e^x - 1) : 1 = (e^{\frac{h\nu}{kT}} - 1) : 1.$$

It follows from this that in absorption of large quanta $h\nu \ll kT$ a basic role is played by bound-free transitions, but in absorption of little quanta $h_\nu \ll kT$, free-free transitions play a basic role.

§ 7. Continuous Absorption of Light in Monatomic Gas in Region of First Ionization

Let us consider continuous absorption of light in monatomic gases, such as inert gases (argon, xenon, and others) or vapor of metals, in region of first ionization. We will assume the gas to be monatomic in order to exclude from consideration quasi-continuous molecular spectra (if dissociation of molecules is almost total, then, obviously, any gas is monatomic).

The region of first ionization lies in range of temperatures of the order of 6000-30,000°K (depending upon ionization potential of atoms and density of gas) and presents great interest in connection with numerous laboratory investigations and practical applications. At higher temperatures second and subsequent ionizations begin, which must be considered in examining absorption; this will be done in the following section.

Let us consider a strongly excited atom as a hydrogen-like system: an "optical" electron (which is one of the outer valence electrons) moves along a great orbit in field of nucleus and remaining electrons. If dimensions of this system of charges, forming "atomic remainder," are small as compared to dimensions of orbit of "optical" electron, which is exactly what happens in the case of great excitations of atom, then it may be presented as point charge $Z = 1$, creating a Coulomb field (if we deal not with a neutral atom, but with an ion, then Z per unit is greater than charge of ion; see following paragraph).

Extending results obtained for hydrogen-like atoms to complex atoms, it is natural by ionization potential in formulas to understand the true potential of a given atom.

Really, the basic factor determining temperature dependence of coefficient of absorption of quanta, considerably smaller than ionization potential, is Boltzmann factor $\exp[-(I - h\nu)/kT]$, to which is proportional the number of atoms, excited somewhat, so that quantum is in state to pull an electron from them. This factor, undoubtedly assists absolutely regardless of whether it is a hydrogen-like atom or a complex atom. One of the co-factors of Boltzmann factor, $\exp(-I/kT)$, describes the degree of ionization, or more exactly, product N_+N_e, to which is proportional coefficient of deceleration absorption, furthermore independently of the type of atom.

In complex atoms each of the "hydrogen-like" levels with given prime quantum number n is split somewhat in accordance with its own statistical weight. This is connected with the fact that in complex atoms due to deflections of field from Coulomb field l-degeneration is absent, and energy of levels with given prime quantum number n, but different orbital numbers l do not coincide (in distinction from hydrogen-like atoms).

If one were to consider such "reproduction" of levels in complex atoms, which leads to appearance of a large number more closely located "teeth" in "paling" of curve $\varkappa(\nu)$, then replacement of summation over levels by integration or replacement of "paling" by an averaged smooth curve is even more natural than in the case of hydrogen-like atoms (Unsöld [10]).

Absorption of small quanta, considerably smaller than ionization potential, apparently, should be not badly described by formula (5.44), derived for hydrogen-like atoms, where for neutral atoms one should consider Z equal to one. Really, the high levels, only from which electrons are pulled by small quanta, in complex atoms are very close to "hydrogen-like," since the field at large distances from the atomic remainder is very close to a Coulomb field.

Regarding large quanta, which are absorbed by atoms, which are in ground or low states, use here of formula (5.44) can, of course, lead to considerable errors.*

Formula (5.44) becomes in general, senseless when energies of quanta exceed ionization potential $h\nu > I$, $x > x_1$. In this case in the sum over n participate all levels from $n = 1$ to ∞ and formula (5.43) with variable lower limit of integration loses its meaning. The sum over levels in this case is simply constant and does not depend

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*See § 5, p. 360, where results are given of calculation of absorption cross section of quanta by certain atoms, which are in the ground state.

on ν (from x). An overwhelming role in absorption of quanta $h\nu > I$ is played by atoms which are in the ground state, and approximately the sum may be considered equal to first member, i.e., unity. This gives approximate formula

$$\varkappa_\nu = \frac{32\pi^2}{3\sqrt{3}} \frac{e^6 Z^2 N}{h^4 c \nu^3} I = 0{,}96 \cdot 10^{-7} \frac{NZ^2}{T^{\circ 2}} \frac{2x_1}{x^3} \; c\text{м}^{-1}$$

$$\text{when } x > x_1, \; h\nu > I, \tag{5.45}$$

which should replace formula (5.44) when $h\nu > I$.

Let us find average Rosseland run of monatomic gas in region of first ionization. The Rosseland run is determined by reciprocal of coefficient of absorption, i.e., transmission.

Spectral range $l_\nu = 1/\varkappa_\nu$, characterizing transmission is schematically depicted in Fig. 5.7. Frequency domains of transmission are opposite regions of absorption and are near discontinuities on the side of smaller frequencies. In energy band of $h\nu$ quanta, exceeding ionization potential, there is practically no transmission, since these quanta are very strongly absorbed by atoms remaining in the ground state.

A basic contribution in transfer of radiant energy is given by quanta corresponding to maximum of weighting function in Rosseland integral (2.80) $x = h\nu/kT \approx 4$. If temperature is considerably less than ionization potential, as usually occurs in region of first ionization of a not too dense gas, absorption of such quanta can approximately be described by formula (5.44), which is more exact the less $h\nu$ is and which it is possible to use for calculation of mean path ("paling" of transmission by this formula is replaced by smooth curve $x^3 e^{-x}$, depicted in Fig. 5.7 by the dotted line).

Inasmuch as large frequencies $x > x_1$ introduce practically no contribution in Rosseland integral (2.80), it is possible to calculate

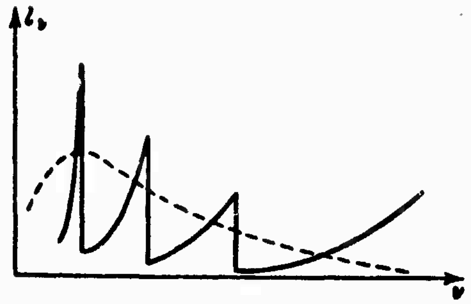

Fig. 5.7. "Paling" of transmission. Solid curve is range as a function of frequency. The dotted curve is a run, smoothed along teeth. Figure is schematic.

this integral, extending formula (5.44), having a meaning only when $x < x_1$, also to $x > x_1$. Actually, formula (5.44) formally ensures very rapid damping of transmission when $x > x_1$, $x \to \infty$. Putting expression (5.44) in Rosseland integral (2.80), we will obtain Rosseland path *

$$l = 0{,}9\cdot10^7 \frac{T^{\circ 2}}{NZ^3} e^{\frac{I}{kT}} \text{ см.} \tag{5.46}$$

It is necessary to note that if one were to calculate Rosseland path with coefficient of absorption, taken not by formula (5.44), but according to the "exact" formula for hydrogen-like atoms (5.42), i.e., without replacement of "paling" of transmission by a smooth curve, values of the path are obtained five larger than formula (5.46) gives (when $x_1 = \frac{I}{kT} \sim 10$).

Let us make, for example, calculations of Rosseland path by the formula of (5.46). For hydrogen when $T = 11{,}600^\circ K = 1$ ev, $N = 10^{19}\text{cm}^{-3}$ we will obtain $l = 100$ cm (degree of ionization under these conditions equals 0.02).

If one were to formally calculate by the formula of (2.105) with the help of formulas (5.44), (5.45) average coefficient of absorption, characterizing integral radiating ability of gas $\varkappa_1$, then for corresponding path length we will obtain

$$l_1 = \frac{1}{\varkappa_1} = 2{,}3\cdot10^7 \frac{T^{\circ 2}}{NZ^3} e^{\frac{I}{kT}} \frac{kT}{I} \text{ см.} \tag{5.47}$$

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*The integral appearing here $\int_0^\infty x^4 e^{-x} G'(x)\,dx$ equals 0.87.

It is necessary, however, to note that this formula can contain a large error, since in integral (2.105) a basic role is played by the region of large frequencies $x > x_1$ for which approximation of hydrogen likeness is the worst of all (basically large quanta are emitted during capture of electrons on ground levels of atoms).

Coefficient of continuous absorption of small quanta, much smaller than ionization potential $kT \ll I$, in region of first ionization when $kT \ll I$ depends on temperature basically according to the law $\varkappa \sim$ $\sim \exp(-I/kT)$, i.e., very sharply. Correspondingly mean path is proportional to $l \sim \exp(I/kT)$. Boltzmann temperature dependence of absorption is characteristic both for is bound-free transitions, and also for deceleration absorption in field of ions, i.e., for both components $\varkappa'_\nu$ and $\varkappa''_\nu$ in $\varkappa_\nu$ (since $\varkappa''_\nu \sim N_+ N_e \sim e^{I/kT}$).

In a number of works are proposed methods to improve Kramer and Kramer — Unsöld formulas, derived for hydrogen-like atoms, during application of them to complex atoms. Instead of charge of "atomic remainder" Z, Unsöld [11] introduces effective charge Z,* which is determined in such a way that magnitude $E_{n.l} = -I_H Z^{*2}/n^2$ corresponds to actual energy level of complex atom with given prime and orbital quantum numbers n and l. Furthermore, the Kramer formula is multiplied by γ/Σ_0, where γ is equal to ratio of number of sublevels of a complex atom for given n and l to analogous magnitude for hydrogen, and Σ_0 is the statistical sum of the atom. Unsöld [11] and others [12] recommend taking for all levels $Z^{*2} \approx 4$-7, corresponding to energy of ground state of atom.

Burgess and Seaton [13], using monoelectron semi-empirical wave functions, found with the help of the method of quantum defect,* obtained general expression for cross section of photo-ionization of arbitrary atom or ion.

L. M. Biberman and G. E. Norman [14], using as a basis the formula of Burgess and Seaton, developed method of approximation of calculation of coefficient of continuous absorption for non hydrogen-like atoms. The coefficient of absorption is presented by them in the form of a formula of the Kramer — Unsöld type in which factor Z^2 is replaced by some function of frequency and, in general, temperature $\xi(\nu, T)$. This function was calculated by them for O, N, C atoms (it approximately does not depend on temperature). Very high levels of atoms always are "hydrogen-like," therefore very little quanta are absorbed just as in hydrogen: when $h\nu \rightarrow 0$ $\xi \rightarrow 1$ (when $Z = 1$).

With increase of energy of quantum from zero to $h\nu \sim 4$ ev coefficient ξ monotonically decreases for these atoms to a magnitude ~1/5. In [15] functions are calculated for a number of other atoms (Li, Al, Hg, Kr, Xe, Ar). For instance, for argon in visible region of spectrum $h\nu \sim 2$-3 ev, $\xi \sim 1.5$-2. Magnitude ξ changes irregularly from atom to atom.

Let us stress once again that the theory of continuous absorption of light by complex atoms and ions at present is in a very imperfect state and existing methods of calculation of coefficients of absorption, apparently, give the only true order of magnitude.

There are experimental indications of the fact that the Kramer —

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*The quantum defect is the magnitude $\Delta n(E_{n,l}) = n - n_l^*$, where n is the prime quantum number for level $E_{n,l}$ of an atom, and n_l^* is the effective number, such that $E_{n,l} = -I_H Z^2/n_l^{*2}$. The quantum defect characterizes deflection of energy level of complex atom or ion from energy of the corresponding level of a hydrogen-like atom.

Unsöld theory gives fair results in application to inert gases. Thus, in the work of A. P. Dronov, A. G. Sviridov and N. N. Sobolev [42] the continuous spectrum of glow of krypton and xenon was studied in a shock tube was studied. The measured intensities will satisfactorily agree with the calculated ones according to the Kramer – Unsöld theory.

It is necessary to note the existence of one more mechanism, which at sufficiently low temperatures certainly should play a predominant role in continuous absorption. It is free-free transitions (deceleration absorption) in field of neutral atoms. The electrical field of a neutral atom, in distinction from the field of an ion, extraordinarily rapidly drops with distance and, essentially, is concentrated only in region of order of dimensions of atom. Nevertheless, a free electron, flying from an atom at very close distance, so to say, piercing the atom, is subjected to the action of this field and can absorb quantum.

The coefficient of deceleration absorption in a field of neutral atoms is proportional to $\varkappa_\nu''' \sim NN_e$. At a small degree of ionization, i.e., at low temperatures, when the number of neutral atoms is practically constant, $\varkappa_\nu''' \sim N_e \sim \exp(-I/2kT)$, whereas coefficient of continuous absorption, considered above, is proportional to $\varkappa_\nu \sim$ $\sim \exp(-I/kT)$. It is clear that at sufficiently low temperatures and a sufficiently small degree of ionization the first magnitude has to become larger than the second while relatively greater the lower the temperature: $\varkappa_\nu'''/\varkappa_\nu \sim e^{I/2kT}$.

Calculations of deceleration absorption in the field of neutral atoms of hydrogen were made by Chandrasekhar and Breen [16]. These calculations show that, as one should have expected, coefficient $\varkappa_\nu'''$, belonging to one atom, is much less than the coefficient of free-free absorption in field of ions $\varkappa_\nu''$, relative to one ion. Thus, for instance, when T = 7200°K for light with wave length λ = 5965 A coefficient $\varkappa_{\nu}'''$, calculated on one atom and one electron, $\varkappa_{\nu}'''/NN_e$ = = $2.5 \cdot 10^{-39}$ cm^5, whereas coefficient $\varkappa_{\nu}''$, calculated on one ion and one electron, equals by formula (5.21) $\varkappa_{\nu}''/N_+N_e = 3 \cdot 10^{-38}$ cm^5. Experimental data for air (see § 21) also indicate that effectiveness of field of neutral atom with respect to deceleration absorption by free electrons is approximately an order less than effectiveness of field of ion.

There is an indication that in the case of heavy atoms, such as mercury, free-free absorption in the field of a neutral atom sharply increases as compared to light atoms (L. M. Biberman and V. Ye. Romanov [17]) and that in heavy monatomic gases this mechanism can play an essential role even during a not very small degree of ionization. However, the quantitative side of this question at present is still not clear.

§ 8. Mean Paths of Radiation During Multiple Ionization of Atoms of Gas

At high temperatures, of the order of several tens of thousands of degrees and higher, atoms of gas are repeatedly ionized. Molecules with such temperatures are completely dissociated so that all gases are "monatomic" and behave in the relation of absorption light in an identical way. Let us find mean paths of radiation in repeatedly ionized gas. (Results put forth below were obtained in the work of author [18]). For simplicity we will consider a gas consisting of atoms of one element.

Calculations of ionization equilibrium show that for every pair of values of temperature and density in gas ions of only two-three charges (see § 7 Ch. III) assist in considerable quantity. Each of these ions introduces its own contribution in continuous absorption, participating both in bound-free, and also in free-free transitions. The same calculations indicate that in a gas of not too great a density, ionization potentials of ions assisting in large quantity, are always much larger than kT. For instance, in air with a density 100 times smaller than normal, the "average" ionization potential of ions I (corresponding to ions with "average" charge at a given temperature and density) is approximately 11 times more than kT. Consequently, quantum with energies $h\nu$, 3-5 times exceeding kT, which play a main role in transfer of radiant energy, are absorbed not from ground, but from excited levels of ions. As also in the case of neutral atoms, this can serve as base for transfer of formulas derived for hydrogen-like atoms to multiply charged ions. Moreover, for multiply-charged ions the approximation of hydrogen similarity is even more justified than for neutral atoms, since the field of "atomic remainder" of a multiply charged ion is nearer to a Coulomb field the larger the charge of the "remainder" is.

Let us consider continuous absorption by multiply charged ions as absorption by hydrogen-like atoms with corresponding charge. Let us assume that in gas containing N nuclei in 1 cm^3 at temperature T, in 1 cm^3 is N_mm times ionized atoms (for brevity, we will call them m-ions). We will set forth the total coefficient of bound-free absorption by m-ions and free-free absorption in field of m + 1-ion by formulas (5.44), (5.45), in which we use charge Z equal to charge of "atomic remainder" of m-ions, $Z = m + 1$, and as ionization potential we will take the true potential of an m-ion — I_{m+1}. Assembly of bound-free and free-free coefficients for multiply charged ions fully corresponds to the same assembly in region of first ionization. Actually, coefficient of free-free absorption in field of m + 1-ions is proportional to the product $N_{m+1}N_e$, which, as earlier, by the formula of Saha (3.44) is expressed through the number of m-ions N_m. Let us write the total coefficient of absorption in the form

$$\varkappa_{\nu m}=\frac{aN_m(m+1)^2}{T^2}e^{-x_{1m}}F_m(x), \tag{5.48}$$

where

$$a=\frac{16\pi^2}{3\sqrt{3}}\frac{e^6}{hck}=0{,}96\cdot 10^{-7}\ \text{cm}^2\text{deg}^2,$$

$$x_{1m}=I_{m+1}/kT,\quad x=h\nu/kT,$$

in $F_m(x)$ is included frequency dependence

$$F_m(x)=\frac{e^x}{x^3}\ \text{when}\ x<x_{1m}. \tag{5.49}$$

For quanta exceeding ionization potential, we will put in accordance with (5.45)

$$F_m(x)=2x_{1m}\frac{e^{x_{1m}}}{x^3}\ \text{when}\ x>x_{1m}. \tag{5.50}$$

In order to obtain total coefficient of absorption of frequency ν, one should sum partial coefficient $\varkappa_{\nu m}$ over all sorts of ions, i.e., over charge m:

$$\varkappa_\nu=\sum_m \varkappa_{\nu m}. \tag{5.51}$$

Let us find before average coefficient of absorption $\varkappa_1$, characterizing integral radiating ability.

Putting spectral coefficient $\varkappa_\nu$ in formula (2.105) and calculating the integral over the spectrum, we will obtain

$$\varkappa_1=\frac{1}{l_1}=\frac{45a}{\pi^4T^2}\sum_m N_m(m+1)^2x_{1m}e^{-x_{1m}}. \tag{5.52}$$

Now we will find average Rosseland path, for which we will place $\varkappa_\nu$ in formula (2.80):

$$l=\frac{T^2}{a}\int_0^\infty\frac{G'(x)\,dx}{\sum_m N_m(m+1)^2e^{-x_{1m}}F_m(x)}. \tag{5.53}$$

Here G'(x) is Rosseland weighting factor. In this expression it is impossible without additional considerations to be free of integration over the spectrum, as during calculation of $\varkappa_1$, since here is averaged not coefficient of absorption, which is additive but is reciprocal. However, integration nevertheless may be conducted approximately. According to the formula of (5.49) all ions in their own band of transmission, i.e., when $x < x_{1m}(h\nu < I_{m+1})$, with change of frequency absorb light equally. Actually the upper limit of integral (5.53) is least of boundaries of transmission, which possess ions assisting in gas in so considerable a quantity that they give a noticeable contribution in absorption.

As was noted above, for every pair of values of temperature and density of gas ions of only two-three charges assist considerably. Inasmuch as average ionization potential $\overline{I}$ is considerably larger than kT, boundaries of transmission of these ions x_{1m} lie beyond the limits of that region of the spectrum which gives an essential contribution in integral (5.53). Therefore it is possible to approximately disregard dependence of function $F_m(x)$ on m and to carry it after the sign of sum over m, and furthermore, to extend expression (5.49) for $F_m(x)$ also to values of $x > x_{1m}$, just as was done in the preceding section. With these simplifications the integral is turned into precisely the same as and in case of neutral atoms (see footnote on p. 370). We obtain

$$l = \frac{0{,}87T^2}{e}\,\frac{1}{\sum\limits_m N_m(m+1)^2 e^{-x_{1m}}}. \qquad (5.54)$$

For approximate calculation of sums over charges of ions in formulas (5.52), (5.54) we will use the method applied in § 7 Ch. III during calculation of thermodynamic functions of gases in region of multiple ionization. We will consider distribution of ions N_m as a temperature in gas are present atoms excited to all possible energies. If N_n is the number of atoms in 1 cm^3, being in n-th quantum state, and $\sigma_{\nu n}$ is the effective absorption cross section of $h\nu$ quantum by these atoms, then coefficient of absorption equals*

$$\varkappa'_\nu = \sum_{n^*}^{\infty} N_n \sigma_{\nu n}. \tag{5.38}$$

The lower limit in this sum is determined from the condition that energy of quantum is larger than binding energy of electron in atom, $h\nu > |E_n|$. Otherwise quantum cannot force out electron and, consequently, atoms excited to states with $n < n,*$ for which $|E_n| > h\nu$, do not participate in absorption of $h\nu$ quanta. In particular, if energy of quantum exceeds binding energy of electron in the ground state of the atom, i.e., ionization potential $I = I_H Z^2$, then in absorption participate all atoms ($n^* = 1$). In absorption of very little quanta $h\nu \ll I_H Z^2$ participate only highly excited atoms ($n^* \gg 1$).

The absorption curve depending upon frequency has the character of "paling," as is shown in Fig. 5.6. As soon as energy $h\nu$, increasing, attains binding energy of electron in any state $|E_n|$, atoms excited before this level, are included in absorption and coefficient of absorption grows by jumps. Then, up to inclusion of the following level, $\varkappa'_\nu$ decreases $\sim\nu^{-3}$, in conformity with the law $\sigma_{\nu n} \sim \nu^{-3}$. Every level introduces its own "tooth" into paling $N_n\sigma_{\nu n}$ (dotted lines in Fig. 5.6), and total coefficient of absorption $\varkappa'_\nu$ is obtained by means of summation of all "teeth" (solid line in Fig. 5.6).

If the gas is in a state of thermodynamic equilibrium, the number of atoms in the n-th state N_n is determined by Boltzmann formula (5.32).

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*Let us note here the coefficient of bound-free absorption by a dash in order to distinguish it from the coefficient of free-free absorption, which will be marked by two dashes.

δ-function around its "average" charge $\overline{m}$, which is determined by equation (3.57).

As was shown in § 7 Ch. III, distribution function of ions N_m has the character of a sharp peak, described by Gaussian curve $N_m \sim$ $\sim \exp[-(m - \overline{m})^2/\Delta^2]$ (see formula (3.58).

If one were to expand factor $e^{-x_1 m}$, which is in the sum of (5.52), (5.54), near mean value $\overline{x}_{1m}$, we find that this factor depends on $m - \overline{m}$ according to the law $e^{-x_{1m}} \approx e^{-\overline{x}_{1m} - \mathrm{const}\,(m - \overline{m})}$, i.e., weaker than N_m. Therefore, application of shown approximate method of calculation of sum over m in this case, just as in § 7 Ch. III, is possible. Carrying mean values of coefficients for N_m in components of sums after sign of summation and taking into account that $\Sigma N_m = N$, we obtain

$$l = \frac{0{,}87T^2}{a}\,\frac{e^{\overline{x}_1}}{N(\overline{m}+1)^2},$$

$$l_1 = \frac{\pi^4 T^2}{45a}\,\frac{e^{\overline{x}_1}}{N(\overline{m}+1)^2\,\overline{x}_1},$$

where $\overline{x}_1 = \overline{x}_{1m} = \overline{I}/kT$.

Using formula (3.56) for replacement of exponent and putting in numerical value of a, we obtain finally:

$$l = \frac{4{,}4\cdot 10^{\text{[illegible]}}T^{\circ\frac{7}{2}}}{N^2\overline{m}(\overline{m}+1)^2}\ \text{см}, \qquad (5.55)$$

$$l_1 = \frac{1{,}1\cdot 10^{\text{[illegible]}}T^{\circ\frac{7}{2}}}{N^2\overline{m}(\overline{m}+1)^2\,\overline{x}_1}\ \text{см}. \qquad (5.56)$$

Average charge $\overline{m}$ and average relative ionization potential $\overline{x}_1 =$ $= \overline{I}/kT$, depending upon temperature and density, are determined by means of solution of equation (3.57).

As a check shows, error connected with approximate calculation of sums over m, is minute; in any case it is less than possible errors connected with use of approximation of hydrogen-similarity in examining of complex ions. It is possible, however, to trust that obtained formulas (5.55), (5.56) give correct order of magnitude of mean paths and truly describe dependence of them on temperature and density of gas.

For illustration of numerical values of mean paths in Table 5.2 are given results of calculation for air.* Unfortunately, dependences $l(T, N)$ and $l_1(T, N)$ in a wide range of change of variables cannot more or less exactly be described by interpolation formula of exponential type, very convenient for practical purposes. In rough approximation indices of degree in the law $l \sim T^{\alpha}N^{-\beta}$ are such: $\alpha \sim 1.5\text{-}3$; $\beta \sim 1.6\text{-}1.9$.

If one were to investigate dependence of mean path on temperature, starting from low temperatures, then it will develop that function $l(T)$ has a minimum.

Table 5.2. Mean Paths of Radiation in Air in Region of Multiple Ionization

T, °K		N/N_{nor} : $N_{nor} = 5{,}34 \cdot 10^{19}$ cm^{-3}		
		1	10^{-1}	10^{-2}
50 000	$\bar{m}$	1,4	1,85	2,35
	l, см	0,053	2,8	170
	l_1, см	0,02	0,8	39
100 000	$\bar{m}$	2,72	3,47	4 1
	l, см	0,13	7	470
	l_1, см	0,05	2	110
250 000	$\bar{m}$	4,85	5,15	5,2
	l, см	0,72	61,5	6000
	l_1, см	0,24	15,6	1200
500 000	$\bar{m}$	5,2	5,4	5,85
	l, см	6,8	610	50 000
	l_1, см	2,0	140	9500

In region of single ionization, when $kT \ll I_1$, $l \sim e^{\frac{I_1}{kT}}$ (see formula (5.46)), i.e., very rapidly decreases with increase of temperature. The path becomes minimum in the region where second ionization begins (in air when T ~ 20,000-40,000°K). After that it increases during temperature rise, at first slower than $T^{7/2}$, and then, during

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*In the table given in [18], error was allowed. All values of paths l and l_1 were understated uniformly by 10 times.

total ionization when there remains only the deceleration mechanism, in proportion to $T^{7/2}$ (see formula (5.24)). It is necessary to note that growth of Rosseland path is not infinite: with very small absorptions light scattering becomes essential (see § 2 Ch. II), which was not considered in calculations. The range for Compton scattering of quanta $h\nu \ll mc^2 = 500$ kev in air of normal density equals 37 m. This also is the upper limit of the Rosseland path at normal air density. Let us stress that character of dependencies $l(T, N)$, $l_1(T, N)$ and order of magnitude of paths in region of multiple ionization for all gases are approximately identical, since potentials of consecutive ionizations for all elements are more or less similar to one another.

Let us estimate, for example, radiating ability and speed of radiant cooling of a transparent particle of air with dimensions $R \ll l_1$. When $T = 50{,}000^\circ K$ and $N = 10^{-2} N_{nor}$ $l_1 = 39$ cm, $J = 4\sigma T^4/l_1 = 3.6 \cdot 10^{13}$ erg/cm^{3}sec. Internal energy of air in these conditions $\varepsilon = 83$ ev/atom. Initial scale of time of cooling $\tau = N\varepsilon/J$ is $\tau = 1.9 \cdot 10^{-6}$ sec $\left(\frac{d(N\varepsilon)}{dt} = -J\right)$.

2. Line Spectrum of Atoms

§ 9. Classical Theory of Spectral Lines

Line spectra are emitted and are absorbed as a result of bound-bound transitions in atoms (ions), i.e., during transitions of an atom from one energy state to another.

In the classical theory a model of radiating atom is an elastically bound electron, which vibrates near a certain position of equilibrium. In zero approximation, without taking into account losses of energy on radiation, such a system constitutes a harmonious oscillator. Inasmuch as a vibrating electron moves acceleratedly, it radiates light. If loss of energy after a period of one vibration is very small as compared to the actual energy of vibrations W, then speed of radiation can be calculated after the general formula (5.1), placing in it acceleration of harmonious oscillator. Let us designate by ν_0 the natural frequency of the oscillator. If r is coordinate of electron, counted off from position of equilibrium, then acceleration is $w = 4\pi^2\nu_0^2 r$. Time average speed of loss of energy of electron on radiation according to (5.1) equals

$$\frac{dW}{dt} = -S = -\frac{32\pi^4}{3}\frac{e^2}{c^3}\nu_0^4\langle r^2\rangle = -\frac{32\pi^4}{3}\frac{\nu_0^4}{c^3}\langle d^2\rangle, \tag{5.58}$$

where d = er is the dipole moment. Symbol <> signifies time average. Expressing average square of deflection of electron $\langle r^2\rangle$ by energy of oscillator W, we will obtain the energy radiated in 1 sec:

$$S = -\frac{dW}{dt} = \frac{8\pi^2 e^2}{3mc^3}W = \gamma W. \tag{5.59}$$

The combination

$$\gamma = \frac{8\pi^2 e^2\nu_0^2}{3mc^3} = 2{,}5\cdot 10^{-22}\nu_0^2\,\frac{1}{\text{sec}} \tag{5.60}$$

is the reciprocal of the time during which energy of oscillator decreases e times (if initial energy of oscillator equals W_0, then $W = W_0 e^{-\gamma t}$). The magnitude γ is called the attentuation constant.

The condition of weak damping $\gamma \ll \nu_0$, lying at the basis of derivation of formula (5.58), is always executed with great accuracy.* Thus, for instance, for violet light $\lambda = 4{,}000$ Å, $\nu = 7.5\cdot 10^{14}$ sec^{-1} ($h\nu = 3.1$ ev), and $\gamma = 1.4\cdot 10^8$ sec^{-1}; $\tau = 1/\gamma = 0.7\cdot 10^{-8}$ sec.

If we calculate losses of energy on radiation, then in the following approximation the oscillator accomplishes no longer harmonious, but damped oscillations, whose amplitude is proportional to $\sqrt{W} = \sqrt{W_0}e^{-\frac{\gamma t}{2}}$. Consequently, radiated now is not natural frequency ν_0,

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*Using quantum ideas, this condition can be rewritten in the form $\frac{8\pi^2 e^2\nu_0^2}{3mc^3} \ll \nu_0$; $h\nu_0 \ll \frac{3}{8\pi^2}\frac{hmc^3}{e^2} = \frac{3}{4\pi}\frac{hc}{2\pi e^2}mc^2 = \frac{3}{4\pi}\cdot 137\cdot mc^2 = 163$ Mev.

but the whole spectrum of frequencies. In order to find spectral composition of radiation, it is necessary to expand into a Fourier integral the acceleration of the oscillator (is assumed that when $t < 0$ there is no motion and $\mathbf{r} = 0$, $\mathbf{w} = 0$). Energy radiated throughout the time in spectral interval $d\nu$, $S_\nu d\nu$, will be determined through Fourier-component of acceleration by formula (5.4). Calculation, which can be found in [19], yields when $\nu - \nu_0 \ll \nu_0$:

$$S_\nu d\nu = \frac{2e^2\nu_0^2}{3mc^3}\frac{W_0}{(\nu-\nu_0)^2+\left(\frac{\gamma}{4\pi}\right)^2}d\nu. \qquad (5.61)$$

It is easy to check, integrating this expression over the whole spectrum from $\nu = 0$ to $\nu = \infty$, that total energy is equal to initial energy of oscillator:

$$\int_0^\infty S_\nu d\nu = \int_0^\infty S\,dt = \int_0^\infty \gamma W_0 e^{-\gamma t}\,dt = W_0.$$

Is possible to speak about energy radiated by oscillator in frequency interval $d\nu$ in 1 sec. This magnitude equals $\gamma S_\nu\,d\nu$, where in expression (5.61) instead of W_0 it is necessary in this case to write W as energy of oscillator in given moment of time.

Spectral distribution of radiation of fading oscillator, which is expressed by formula (5.61), is depicted in Fig. 5.8. Half-width of peak, so called natural width, whose meaning is clear from Fig. 5.8, equals $\Delta\nu = \gamma/2\pi$.

In scale of wave lengths the natural width does not depend on wave length and equals $\Delta\lambda = \frac{c\Delta\nu}{\nu_0^2} = \frac{4\pi}{3}\frac{e^2}{mc^2} = \frac{4\pi}{3}r_0 = 1.2\cdot 10^{-4}$ Å$\left(r_0 = \frac{e^2}{mc^2} = 2.8\cdot 10^{-13}\right.$ cm — "radius of electron)."

Above was considered the inadvertent emission of light to a once excited oscillator. Let us assume that now on the oscillator from without falls monochromatic light wave of frequency ν with amplitude constant in time. Under action of electrical field of wave the elastically bound electron performs forced vibrations. If there was no damping, the light wave in a short time after the moment of its "inclusion" would excite the oscillator, imparting to it a specific energy, and after that (on the average with respect to time) would not produce work. If, however, there is damping, forced vibrations are accompanied by continuous radiation of energy by oscillator. This energy is drawn out owing to work producible by external field.

Let us find work accomplished by periodic field of light wave above oscillator. Let us solve for this the equation of motion of an oscillator:

$$m\ddot{r} + m(2\pi\nu_0)^2 r + m\gamma\dot{r} = eE_0 e^{i2\pi\nu t}.$$

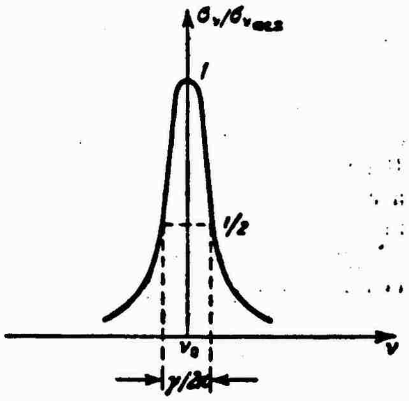

Fig. 5.8. Form of line of absorption.

Here E_0 is the amplitude of electric field strength. Term $m\gamma\dot{r}$ considers "frictional force" connected with damping. Solution of this equation has the form

$$r = r_0 e^{i2\pi\nu t}, \quad r_0 = \frac{1}{4\pi^2}\frac{e}{m}E_0\frac{1}{\nu_0^2-\nu^2+i\nu\frac{\gamma}{2\pi}}. \qquad (5.62)$$

Work accomplished by external force in 1 sec is equal to product of force by speed $\dot{\mathbf{r}}$. Multiplying equation of motion by $\dot{\mathbf{r}}$ and averaging with respect to time, as a result of which terms $\langle \ddot{r}\,\dot{r}\rangle$ and $\langle r\,\dot{r}\rangle$ disappear, we will find that work in 1 sec equals

$$\langle eE_0 e^{i2\pi\nu t}\dot{r}\rangle = 2\pi^2 m\gamma\nu^2 |r_0^2|. \qquad (5.63)$$

It is determined by modulus of complex value $\mathbf{r}^2$.

Work is equal to energy which is taken away by oscillator from light wave in 1 sec, i.e., is absorbed by oscillator.

Leaving for now the question about further fate of the absorbed energy, we will calculate effective absorption cross section. It, by definition, equals the energy absorbed in 1 sec divided by average energy flow of light wave with respect to time. Average flux equals $\frac{c}{4\pi} E_0^2$. Thus, we will obtain effective absorption cross section of light of frequency ν. At frequencies ν, not too far from resonance $|\nu - \nu_0| \ll \nu_0$, it is equal to

$$\sigma_\nu = \frac{e^2}{mc} \frac{\gamma}{4\pi} \frac{1}{(\nu - \nu_0)^2 + \left(\frac{\gamma}{4\pi}\right)^2}. \tag{5.64}$$

If damping of vibrations of oscillator is connected exclusively with radiation, then all energy is expended on emission of light. In this case we deal essentially, not with absorption of light, but with its scattering (in classical theory). The attenuation constant here is expressed by formula (5.60).*

For effective attenuation cross section of incident light wave by oscillator we will obtain in this case by formula (5.64):

$$\left.\begin{aligned} \sigma_\nu = \frac{4{,}23\cdot 10^{-10}}{\nu_0^2} \frac{1}{1+\xi^2}\ \text{см}^2 = \frac{7{,}2\cdot 10^{-9}}{(h\nu_{0e})^2} \cdot \frac{1}{1+\xi^2}\ \text{см}^2, \\ \xi = \frac{(\nu - \nu_0)}{(\gamma/4\pi)}. \end{aligned}\right\} \tag{5.65}$$

In center of line the effective cross section is equal to $\sigma_{\nu_{max}} = \frac{3}{2\pi} \lambda^2$ or $\sigma_{\nu_{max}} = 7.2\cdot 10^{-9}/(h\nu_{ev})^2 \cdot \text{cm}^2$ ($\lambda = c/\nu$ is wave length of light). This cross section is very great. For visible light $h\nu \sim 2$-3 ev $\sigma_{\nu\ max} \sim 10^{-9}$ cm^2, which corresponds to mean free path of light $l \sim 10^{-10}$ cm during atmospheric density of atoms $N \sim 10^{19}$ 1/cm^3.

An excited oscillator can lose its own energy also because of collisions of atoms with each other. In this case absorbed energy of light wave partially passes into heat. It is possible to show (see [19]), that also in this case vibrations of oscillator are described by formula (5.62), but only by γ should one now understand not natural

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*Putting in (5.58) the solution of (5.62), we will obtain $S = \frac{2}{3} \frac{e^2}{c^3} (2\pi\nu)^4 \frac{(r_0^2)}{2}$. Equating this expression (5.63), we will obtain formula (5.60) for attenuation constant.

width line (5.60), but sum of natural width and magnitude $2/\tau_{col}$, where τ_{col} is average time between collisions leading to "deactivation" of oscillator. Formula (5.64) preserves its own form in exactly the same way for effective absorption cross section, if by γ we understand total line width, widened due to collisions.

The fate of absorbed energy of light is determined by relationship between natural width γ and reverse time between collisions $2/\tau_{col}$. If $\gamma >> 2/\tau_{col}$, which occurs in a very rarefied gas, then absorbed energy is illuminated (light is dispersed); if, however, $\gamma << 2/\tau_{col}$ – energy passes basically into heat (absorption in the literal meaning of the word). There exist also other mechanisms of broadening spectral lines in gas (see [6, 10, 19]).

Let us assume that in an "atom" there are f_k oscillators with frequency ν_{0k}, and number of atoms in 1 cm^3 equals N. Total coefficient of absorption of light of frequency ν then equals

$$\varkappa_{\nu} = N \sum_{k} f_k \sigma_{\nu k}. \tag{5.66}$$

Usually individual lines ν_{0k} will stand from each other at a distance much larger than the line width. An overwhelming role in absorption of light of a given frequency is played by oscillators with natural frequency ν_0, the closest to the absorbed, and in sum (5.66) there remains actually only one term. Inasmuch as lines are extraordinarily narrow, there are absorbed, essentially, only frequencies very close to natural frequencies of oscillators: absorption has a selective character. Let us assume that on the atoms falls a continuous spectrum of radiation with density of energy U_ν, which, as usually occurs, changes little in interval of frequencies of the order of the line width. Total energy content absorbed in 1 sec in 1 cm^3 by oscillators with frequency ν_0, equals $\int_0^\alpha U_\nu \, d\nu \, c \, N\sigma_\nu f = U_\nu cNf \int_0^\infty \sigma_\nu \, d\nu$

(index k is omitted). Absorption on one atom is characterized by a magnitude obtained by means of integration of cross section of (5.64). For one line the integral from the cross section with respect to frequency, i.e., area of line, equals

$$f\int_0^\infty \sigma_\nu\, d\nu = \frac{\pi e^2}{mc} f = 2{,}64\cdot 10^{-2} f \text{ cm}^2\cdot\text{sec}^{-1}. \tag{5.67}$$

This is constant, depending only on number of oscillators f and not depending on line width. Therefore, if line is widened, for instance, owing to collisions, then effective cross section now will be less than for a line with natural width.

Absorption of light by oscillator depends on frequency exactly as radiation does (cf. formula (5.61) and (5.64)). This is in accordance with principle of detailed balancing, fulfillment of which is easy to check by means of direct calculation.*

§ 10. Quantum Theory of Spectral Lines. Vibration Strength

Let us consider radiation and absorption of light from the quantum-mechanical point of view.

Between results of quantum and classical theories there is a deep-seated parallelism. In zero approximation of quantum theory of atom, corresponding to steady states, only strictly defined levels of energy of atom are possible (analogous to constancy of energy of sustained vibrations of classical). In the following approximation appears possibility of transitions between energy states of atom. In virtue of the fact that states are non-stationary, according to indeterminancy

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*$\gamma S_\nu\, d\nu = U_\nu c\, d\nu\, \sigma_\nu$; this relationship is satisfied, if one places W and U_ν thermodynamic equilibrium values of energy of oscillator (three-dimensional) and density of radiation, either according to the classical theory: $W = 3kT$, $U_\nu = 8\pi\nu^2 kT/c^3$ or according to the quantum theory.

principle levels of energy (besides ground) turn out to be blurred on magnitude $\Delta E \sim h/\Delta t$, where Δt — "life" of atom in considered state — equal to reciprocal of probability of spontaneous transitions to lower levels. But blurring of levels leads also to blurring of lines on a magnitude of the order $\Delta\nu \sim \Delta E/h \sim 1/\Delta t$, i.e., order of constant "damping" $1/\Delta t$, as also in classical theory. Width of n-th energy level is equal, in accordance with what was said, to the sum of probabilities of transitions to all lower levels,

$$\Gamma_n = \sum_{n'} A_{nn'}, \tag{5.68}$$

where $A_{nn'}$ $\sec^{-1}$ is the probability of spontaneous transition $n \to n'$, so called coefficient of Einstein for emission.

Quantum mechanics gives for speed of radiation the magnitude

$$S = h\nu_{nn'} A_{nn'} = \frac{64\pi^4}{3} \frac{\nu_{nn'}^4}{c^3} |d|^2, \tag{5.69}$$

where $|\mathbf{d}|$ is matrix element of dipole moment. Expression (5.59) is very similar to classical expression (5.58); the difference consists only in replacement of mean square of dipole moment by doubled square of matrix element of the same moment. Numerical values of probability of radiation $A_{nn'}$, have the same order as classical "probability," i.e., attenuation constant γ.

Table 5.3. Probability of Transitions in Atom of Hydrogen in Units of 10^8 $\sec^{-1}$

Initial state	Final state	$n=1$	$n=2$	Sum	Life 10^{-8} sec
$2s$	np	—		0	
$2p$	ns	6,25		6,25	0,16
2	Average	4,69			
$3s$	np	—	0,063	0,063	16
$3p$	ns	1.64	0,22	1,86	0,54
$3d$	np	—	0,64	0,64	1,56
3	Average	0,55	0,43	0,48	1,02

In Table 5.3 are given values of $A_{nn'}$ for certain transitions in atom of hydrogen* (for a diagram of levels see in Fig. 2.2 and 5.9). Knowing coefficients of probability $A_{nn'}$, it is easy to calculate intensity of corresponding lines of emission. Namely, if N_n is the number of atoms in 1 cm^3, remaining in n-th state, which can be calculated by the formula of Boltzmann, then energy radiated in line $\nu_{nn'}$ in 1 cm^3 in 1 sec equals $N_n A_{nn'} h\nu_{nn'}$.

The principle of detailed balancing establishes a bond between probabilities of absorption and emission of light for given transition $n \rightleftarrows n'$. Energy absorbed in 1 sec in 1 cm^3 by atoms which are in state n' with their transition into n-th state, equals

$$\int U_\nu c\, d\nu\, \sigma_{\nu_{n'n}} N_{n'} = N_{n'} U_\nu c \int \sigma_{\nu_{n'n}} d\nu = N_{n'} U_\nu c h\nu_{nn'} B_{n'n},$$

where $\sigma_{\nu_{n'n}}$ is the effective absorption cross section of frequency ν within limits of given transition $n' \rightarrow n$, and $B_{n'n}$ is the coefficient characterizing total absorption in given line (so-called coefficient of Einstein for absorption). It is proportional to "area" of line

$$B_{n'n} = \frac{1}{h\nu_{nn'}} \int \sigma_{\nu_{n'n}} d\nu. \tag{5.70}$$

Multiplying speed of absorption by $(1 - e^{-h\nu/kT})$ in order to consider forced emission (see § 4 Ch. II), equating obtained expression of speed of emission and substituting density of radiation U_ν according to the formula of Planck, and number of atoms N_n according to the formula of Boltzmann, we will obtain bond of coefficients of Einstein:

$$A_{nn'} = \frac{8\pi ch\nu^3_{nn'}}{c^3} \frac{g_{n'}}{g_n} B_{n'n}. \tag{5.71}$$

Here g_n, $g_{n'}$ are statistical weight of n- and n'-energy states of atom. Usually it is accepted to characterize absorbing ability of atom in given line $\nu_{nn'}$, determined by area of line $\int \sigma_{\nu n'n} d\nu$, by the number $f_{n'n}$, equal to that number of classical oscillators with

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*These data are taken from book of Bete and Solpiter [5].

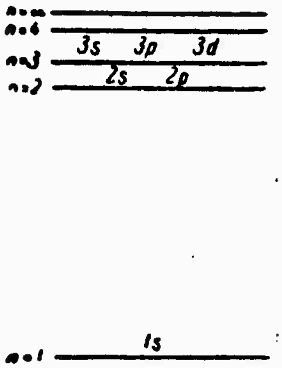

Fig. 5.9. Diagram of levels of atom of hydrogen.

natural frequency $\nu_{nn'}$ which would give the same effect as the considered atom. This number $f_{n'n}$ is called oscillator strength for a given transition and now no longer is an integer. Comparing area of line by formulas (5.70) and (5.67) and considering (5.71), (5.60), we will find bond between oscillator strength and coefficients of Einstein, which, in essence, are determinations of idea of oscillator strength:

$$B_{n'n}=\frac{\pi e^2}{mc}\frac{1}{h\nu_{nn'}}f_{n'n}, \tag{5.72}$$

$$f_{n'n}=\frac{1}{3}\frac{g_n}{g_{n'}}\frac{A_{nn'}}{\gamma}.^{*} \tag{5.73}$$

Regarding distribution of absorption with respect to frequency within limits of line, the quantum theory leads to the same dependence of probability of absorption of quantum on frequency, as the classical formula for cross section σ_ν. Standardizing this probability in the appropriate way, it is possible to write the quantum formula for absorption cross section in a form analogous to that of the classical formula (5.64) (we will transpose indices n and n', i.e., will designate by n the lower state from which transition is accomplished with absorption of quantum),

$$\sigma_{\nu nn'}=\frac{e^2}{mc}\frac{\Gamma_{nn'}}{4\pi}f_{nn'}\frac{1}{(\nu-\nu_{nn'})^2+\left(\frac{\Gamma_{nn'}}{4\pi}\right)^2}. \tag{5.74}$$

If one were to substitute here the value of $f_{nn'}$ according to formula (5.73), using expression for γ, and to consider that $c/\nu = \lambda$, the cross section can be written in the form

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*Let us note that the number $f_{n'n}$ determined by formulas (5.72) or (5.73) constitutes average oscillator strength calculated on one degree of freedom of electron. Full oscillator strength is three times larger in accordance with the fact that an electron in an atom possesses three degrees of freedom.

$$\sigma_{\nu nn'}=\frac{\lambda^2}{8\pi^2}\frac{g_n}{g_{n'}}A_{n'n}\frac{\Gamma_{nn'}}{4\pi}\frac{1}{(\nu-\nu_0)^2+\left(\frac{\Gamma_{nn'}}{4\pi}\right)^2}=$$

$$=\sigma_{\nu nn'\max}\frac{(\Gamma_{nn'}/4\pi)^2}{(\nu-\nu_0)^2+(\Gamma_{nn'}/4\pi)^2},$$

where cross section in center of line:

$$\sigma_{\nu nn'\max}=\frac{\lambda^2}{2\pi}\frac{g_n}{g_{n'}}\frac{A_{n'n}}{\Gamma_{nn'}}.$$

Line width (natural) in quantum theory is put together from probabilities of transitions (5.68): $\Gamma_{nn'} = \Gamma_n + \Gamma_{n'}$.* In accordance with determinations of oscillator strength and coefficient of Einstein $B_{nn'}$ and (5.72), (5.70), area of line equals

$$\int\sigma_{\nu nn'}\,d\nu=\frac{\pi e^2}{mc}f_{nn'}=2{,}64\cdot 10^{-2}f_{nn'}\ \mathrm{cm}^2\cdot\mathrm{sec}^{-1}.$$

It absolutely does not depend on line width $\Gamma_{nn'}$, in which in the presence of collisions is included also the term $2/\tau_{col}$. This is very natural, since area of line by the principle of detailed balancing is simply connected with probability of spontaneous emission, which, of course, cannot depend on such external causes as collision of atoms, and is determined only by structure of the actual atom.

Usually in real gas there exists a series of causes according to which spectral lines expand: collision of atoms with each other, Doppler effect, Stark-effect.** Thus, broadening due to collisions adds to natural line width γ a magnitude equal to doubled probability of collisions $\gamma_{col} = 2/\tau_{col}$. For instance, in air during normal conditions the time between collisions of molecules $\tau_{col} \sim 0.74\cdot 10^{-9}$ sec and $\gamma_{col} = 2.7\cdot 10^9$ sec^{-1},***which is an order larger than attenuation

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*In width of levels Γ_n, $\Gamma_{n'}$, are included also probabilities corresponding to forced emission. These terms are proportional to density of radiation and are essential only with sufficiently large densities.

**For greater detail about broadening of lines, see [6, 10, 19].

***Strictly speaking, one should take into account not any collisions, but only those which lead to deactivation of excited atoms.

constant γ for ultraviolet radiation. Correspondingly, line width also increases by an order. Doppler broadening equals approximately $\Delta\nu = \nu\bar{v}/c$, where $\bar{v}$ is rate of thermal motion. When $\bar{v} = 4.6\cdot 10^{4}$ cm/sec (velocity of molecules of air at normal temperature) for line $\lambda = 4{,}000$ Å $\nu = 7.5\cdot 10^{14}$ sec^{-1}, $\Delta\nu = 1.15\cdot 10^{9}$ sec^{-1}, i.e., also considerably larger than natural width.

§ 11. Absorption Spectrum of Hydrogen-Like Atoms

Let us assume that on a gas from hydrogen-like atoms (in particular, on atomic hydrogen) from without falls light with a continuous spectrum in which all frequencies are represented. Let us consider which of these frequencies will be absorbed by atoms remaining in a specific n-th, state, and what intensity of absorption will be.

Atoms selectively absorb frequencies $\nu_{nn'}$, corresponding to transitions of electron from n-th level to higher levels $n' > n$. Having in mind formula (5.25) for energy level, we will find bond of these frequencies with quantum numbers n and n', so-called series formula of Balmer:

$$\nu_{nn'} = \frac{I_H Z^2}{h}\left(\frac{1}{n^2} - \frac{1}{n'^2}\right) = \nu_1\left(\frac{1}{n^2} - \frac{1}{n'^2}\right), \tag{5.75}$$

where $\nu_1 = I_H Z^2/h = \nu_R Z^2$. Frequency $\nu_R = I_H/h = 3.27\cdot 10^{15}$ sec^{-1} corresponds to ionization potential of an atom of hydrogen. It is frequently used as the unit of frequency called "Rydberg." During growth of n' levels and correspondingly, $\nu_{nn'}$ lines are rapidly compressed and in limit $n' \to \infty$ pass into continuum (continuous spectrum), since during absorption of frequencies exceeding upper limit of series $\nu_n = \nu_{n,\infty} = \nu_1/n^2$, ionization occurs, and final state of electron falls into continuous spectrum of energies. Spectrum of absorption from given level of atom n is depicted in Fig. 5.10 (in the same place for comparison is given diagram of levels). For definity it is assumed that n = 1, i.e., figure depicts absorption spectrum of cold gas from hydrogen-like atoms, in which all atoms are in the ground state. In heated gas levels are excited and absorption spectrum constitutes totality of series corresponding to absorption by atoms which are in different states.

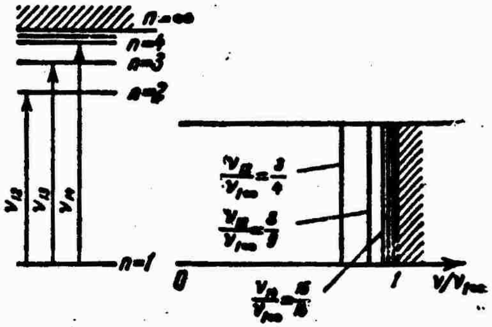

Fig. 5.10. Absorption spectrum of light by atom of hydrogen which is in the ground state. On the left is diagram of transitions.

Near upper boundary of series, where lines are strongly compressed, overlapping of individual lines begins. This occurs when frequency distance between lines, which decreases when $n' \rightarrow \infty$, becomes comparable with width of lines. Overlapping of lines promotes their broadening owing to collisions, Doppler effect etc.

It is easy to see that overlapping of atomic lines begins during such large quantum numbers n' and $\nu_n = \nu_{n\infty}$ series, so close from upper boundary that all this frequency domain of overlapped levels is very narrow and practically does not play a role. In real atomic gas it never exists due to cutting of upper levels owing to interaction of atoms and effective lowering of ionization potential. Thus, for instance, for width of lines $\Delta\nu \sim 10^9$ sec^{-1} their overlapping starts when $n' \approx 200$, at distance $\Delta\nu' = \nu_1/n'^2 = 2.5 \times 10^{-5}\nu_1$ from boundary of continuous spectrum (in scale of wave lengths $\Delta\lambda' \approx 0.02$A).

Actually overlapping of individual lines can appear only during absorption of light by molecules, where the number of lines is much larger than in atoms, and they are located much nearer to one another (see more about this lower).

Let us consider transitions $n \rightarrow n'$ with absorption of light between high levels with large quantum numbers. Motion of electron on such levels is quasiclassic, and absorption of light accompanied by $n \rightarrow n'$ transitions from $n, n' \gg 1$, can be studied using semiclassical concepts.

In spectral region corresponding to transitions from $n, n' \gg 1$, where lines are located very frequently and are almost overlapped, it is natural to smooth dependence of effective absorption cross section on frequency by means of introduction of averaged cross section. Averaging should be done in such a way that total area of lines, which characterizes flux depression of external radiation with continuous spectrum, remains constant.

Let us consider the small spectral interval from ν to $\nu + \Delta\nu$ such that in it is contained many lines, but these lines differ little from each other. Furthermore, we will assume that the interval $\Delta\nu$ is much larger than width of individual line. Effective absorption cross section of frequency ν by atoms which are in the n-th state is equal to $\sigma_{\nu n} = \sum_{n'} \sigma_{\nu nn'}$.

We will average the cross section in interval $\Delta\nu$:

$$\int\limits_{\nu}^{\nu+\Delta\nu} \sigma_{\nu n}\, d\nu = \bar{\sigma}_{\nu n}\, \Delta\nu = \sum_{n'} \int \sigma_{\nu nn'}\, d\nu = \sum_{n'} \frac{\pi e^2}{mc} f_{nn'}.$$

Let us average also oscillator strengths, determining average value $\bar{f}_{nn'} = f_{n\bar{n}'} = f_n(\nu)$ for given interval $\Delta\nu$. If in interval of frequencies from ν to $\nu + \Delta\nu$ are contained lines corresponding to final states from n' to $n' + \Delta n'$, the number of which is equal to $\Delta n'$, then mean cross section can be written in the form

$$\bar{\sigma}_{\nu n} = \frac{\pi e^2}{mc} f_n(\nu) \frac{\Delta n'}{\Delta\nu}. \qquad (5.76)$$

The number of lines on a unit spectral interval can be calculated by means of differentiation of Balmer formula (5.75):

$$\frac{\Delta n'}{\Delta\nu} = \left(\frac{d\nu_{nn'}}{dn'}\right)^{-1} = \left(\frac{2\nu_1}{n'^3}\right)^{-1}. \qquad (5.77)$$

In § 4 we found effective cross section for bound-free transitions, extending the classical expression for effective radiation during free-free transitions to the case when one of the states falls in the discrete spectrum. Justification for such an operation is those considerations that in states with large quantum numbers n motion of an electron is quasiclassic and that motion along "elliptic" orbit, corresponding to large n and small negative energy, is very close to motion along "hyperbolic" orbit with small positive energy. Let us take one more step and consider in that same approximation the case when both states are in the discrete spectrum with large quantum numbers.

Let us consider transitions from n-th level during absorption of quantum in the framework of the same semiclassical concepts. With increase of frequency an electron in the final state falls on an "elliptic" orbit, more and more approaching parabolic; when $\nu = \nu_n$ it falls on a parabolic orbit, and at frequency ν, only a little exceeding ν_n, it falls on a "hyperbolic" orbit, close to parabolic. Inasmuch as motion of electron in final state changes continuously, one should expect that mean effective absorption cross section of light by atoms in n-th state, $\bar{\sigma}_{\nu n}$, also will be continuous during transition from discrete spectrum to continuum.

Let us extend expression (5.34) for cross section of photo-ionization from n-th level to absorption of frequencies of somewhat lower bound of photo-ionization — ν_n,* and equate the cross section of (5.34) to the expression for mean cross section in the case of bound-bound transitions (5.76).

Remembering determination of potential ionization of an atom of hydrogen I_H by formula (5.25) and the expression for frequency boundary of series $\nu_n = \nu_1/n^2$ (see (5.75)), we will find average oscillator

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*Just as in § 4 we extended the expression for effective bremsstrahlung to frequencies somewhat exceeding the highest possible during a free-free transition and, thus, described the photo-capture.

strength $f_n(\nu)$ for transition from n-th level to one of the n'-levels, included in the narrow interval $\Delta n'$, $\Delta\nu$. Designating it by $f_{nn'}$, and frequency ν by $\nu_{nn'}$, we obtain

$$f_{nn'}=\frac{16}{3\pi\sqrt{3}}\frac{1}{n^5}\left(\frac{\nu_1}{\nu_{nn'}}\right)^2\frac{1}{\nu_{nn'}}\frac{\Delta\nu}{\Delta n'}.$$

Substituting here average distance between levels $\Delta\nu/\Delta n'$, calculated by formula (5.77), and replacing frequency of transition $\nu_{nn'}$ according to the formula of Balmer (5.75), we will obtain finally oscillator strength $f_{nn'}$ for transition $n \to n'$:

$$f_{nn'}=\frac{32}{3\pi\sqrt{3}}\frac{1}{n^5 n'^3}\frac{1}{\left(\frac{1}{n^2}-\frac{1}{n'^2}\right)^3}. \tag{5.78}$$

For transitions to levels $n' \gg n$ we will find asymptotic formula:

$$f_{nn'}=\frac{32}{3\pi\sqrt{3}}\frac{n}{n'^3}=\frac{1{,}96n}{n'^3},\quad n'\gg n. \tag{5.79}$$

As can be seen, oscillator strengths depend only on quantum numbers n, n'.

In Table 5.4 are presented oscillator strengths for certain transitions in an atom of hydrogen, calculated by quantum-mechanical means [5].

It is remarkable that semiclassical formulas (5.78), (5.79), derived for the case $n, n' \gg 1$, give a fair estimate even for transitions between levels with small quantum numbers, and also for transitions from ground level. For instance, semiclassical values $f_{12} = 0.585$, $f_{13} = 0.104$, asymptotic $f_{1n'} = 1.96\ n'^{-3}$, and by the table $f_{12} = 0.416$, $f_{13} = 0.079$, asymptotic $f_{1n'} = 1.6 \cdot n'^{-3}$. We here meet the same position as during comparison of semiclassical and quantum cross sections of photo-ionization from ground level of hydrogen-like atom.

Table 5.4. Oscillator Strengths for an Atom of Hydrogen*

Initial state	1s	2s	2p	
Final state	np	np	ns	nd
$n=1$	—	—	−0,139	—
2	0,4162	—	—	—
3	0,0791	0,425	0,014	0,694
4	0,0290	0,102	0,0031	0,122
5	0,0139	0,042	0,0012	0,044
6	0,0078	0,022	0,0006	0,022
7	0,0048	0,013	0,0003	0,012
8	0,0032	0,008	0,0002	0,008
from $n = 9$ to ∞, Σ	0,0101	0,026	0,0007	0,053
Asymptotic formula	$1{,}6 \cdot n^{-3}$	$3{,}7 \cdot n^{-3}$	$0{,}1 \cdot n^{-3}$	$3{,}3 \cdot n^{-3}$
Line spectrum	0,5641	0,638	−0,119	0,923
Continuous spectrum	0,4359	0,362	0,008	0,188
Sum	1,000	1,000	−0,111	1,111

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*Negative oscillator strengths correspond to transitions with emission of quantum. See § 12.

§ 12. Oscillator Strengths for Continuum. Theorem of Sums

In the preceding sections we saw that probability of transitions between discrete levels of atom with absorption of light quanta are characterized by oscillator strengths. By oscillator strength is determined area of line of absorption, i.e., integral with respect to frequencies from effective absorption cross section of light of frequency ν in a given line.

By analogy it is possible to introduce idea of oscillator strength also for bound-free transitions, characterizing by magnitude f_n the integral with respect to frequencies from effective absorption cross section of light with transition of electron from n-th level of atom into continuous spectrum. If $\sigma_{\nu n}$ is the effective cross section of bound-free absorption of frequency ν with such transition, then

$$\int_{\nu_n}^{\infty} \sigma_{\nu_n} d\nu = \frac{\pi e^2}{mc} f_n, \qquad (5.80)$$

where integration with respect to frequencies is conducted from lowest frequency ν_n, at which transition into continuous spectrum is possible.

Let us calculate oscillator strength f_n for bound-free absorption by hydrogen-like atoms.

Using semiclassical formula (5.34) for $\sigma_{\nu n}$ and noticing that $\nu_n = I_H Z^2/hn^2$, we will obtain after integration

$$f_n = \frac{8}{3\pi\sqrt{3}} \frac{1}{n} = \frac{0,49}{n}. \qquad (5.81)$$

Results of quantum-mechanical calculation for an atom of hydrogen are presented in Table 5.4. For instance, for n = 1 the exact value of $f_1 = 0.436$, and by formula (5.81) $f_1 = 0.49$.

In the classical theory every electron participating in radiation and absorption of light is replaced by an oscillator. The sum of numbers of oscillators, consequently, is equal to the prime number of electrons in the atom. The quantum analog of this position is the theorem of sum of forces of oscillators, according to which sum $\Sigma f_{nn'}$ with respect to all allowed transitions in an atom from given state n' n is equal to the number of electrons. If one were to be limited only to transitions with participation of external, optical electrons, then the sum is equal to the number of the latter. In particular, in the case of a hydrogen-like atom the sum is equal to one. In the sum with respect to final states are included also transitions into continuous spectrum, i.e., the term f_n, which, as will be seen below, can be presented in the form of an integral with respect to final states of continuous spectrum. Furthermore, in the sum are included also terms corresponding to transitions to lower levels

$n' < n$, i.e., transitions with emission of light. Corresponding terms of the sum are negative and are determined by probabilities of $A_{nn'}$ transitions (see [5]). Data in Table 5.4, of course, satisfy the rule of sums, which can be checked by means of direct calculation.

In describing bound-free transitions (continuum), and also bound-bound transitions between densely located levels in band spectra of molecules (quasicontinuum) we frequently use the idea of differential oscillator strength or oscillator strength calculated on unit interval of frequencies. Formally, differential oscillator strength $\frac{df}{d\nu}$ is determined in the following way. If σ_ν is absorption cross section of frequency ν during transition from n-th level, then

$$\sigma_{\nu n} = \frac{\pi e^2}{mc}\left(\frac{df}{d\nu}\right)_n = 2{,}64\cdot 10^{-2}\left(\frac{df}{d\nu}\right)_n \text{cm}^2 = 8\cdot 10^{-18}\left[\frac{df}{d(\nu/\nu_R)}\right]_n \text{cm}^2 \tag{5.82}$$

(ν/ν_R is frequency measured in Rybergs).

Hence, total oscillator strength for the whole continuum is defined as

$$\int_{\nu_n}^{\infty}\sigma_\nu\,d\nu = \frac{\pi e^2}{mc}\int_{\nu_n}^{\infty}\left(\frac{df}{d\nu}\right)_n d\nu = \frac{\pi e^2}{mc} f_n \tag{5.83}$$

in accordance with formula (5.80).

Let us calculate differential oscillator strength for bound-free absorption from n-th level of hydrogen-like atom. Comparing formula (5.34) with determination (5.82), we will find

$$\left(\frac{df}{d\nu}\right)_n = \frac{16}{3\pi\sqrt{3}}\frac{1}{n}\frac{\nu_n^2}{\nu^3} = \frac{0{,}98}{n}\frac{\nu_n^2}{\nu^3},\quad \nu_n = \frac{I_H Z^2}{hn^2}. \tag{5.84}$$

Integrating this expression with respect to ν from ν_n to ∞, naturally, we will come to formula (5.81).

If absorption spectrum constitutes totality of many lines, then by cross section $\sigma_{\nu n}$ one should understand mean cross section $\sigma_{\nu n}$ (see formula (5.76)), and the differential oscillator strength is equal to average oscillator strength of one transition, multiplied by the number of lines in a unit interval of frequencies:

$$\left(\frac{df}{d\nu}\right)_n = f_n(\nu)\frac{\Delta n'}{\Delta\nu} = f_n(\nu)\frac{dn'}{d\nu} = f_{nn'}\frac{dn'}{d\nu}. \tag{5.85}$$

In Table 5.5, taken from the book of Unsöld [10], are given forces of oscillators of atoms of hydrogen and alkali metals for continuous spectrum, corresponding to absorption from ground level. There are also values of differential oscillator strength for boundary of absorption $(df/d\nu)_n$ when $\nu = \nu_n$ (ν is measured in Rybergs).

These data are obtained by means of quantum-mechanical calculations. They show degree of "non-hydrogen likeness" of atoms of alkali metals.

Table 5.5. Oscillator Strengths for Continuous Spectrum f and Differential Force $\frac{df}{d\nu}$ for Boundaries of Main Series (ν in Rybergs)

Atom	λ_{margin} Å	f	$\frac{df}{d\nu}$	I (ev)
H	912	0,436	0,78	13,5
Li	2281	0,24	0,46	5,4
Na	2442	0,0021	0,038	5,05
K	2857		0,0024	4,32

§ 13. Remarks About Energy Role of Lines in Radiation of Heated Body and Radiant Transfer of Energy

Above it was noted that energy role of line spectrum in heated gas is small as compared to role of continuous spectrum. During calculation of average Rosseland path and speed of volume cooling only transitions giving a continuous absorption spectrum were taken into account. Now, after we have met regularities of line spectrum, it is possible to explain what causes a similar position. Let us consider radiation of optically thin volume of rarefied gas. According to the law of Kirchhoff radiating ability J_ν is proportional to coefficient of absorption $\varkappa_\nu$, and speed of radiant cooling is proportional to integral over the whole spectrum from coefficient of absorption taken with a specific weight (see formula (2.105)). Let us return to Fig. 5.6, on which is shown "paling" of continuous absorption, and more intently we consider only one, main "tooth" corresponding to absorption from ground level n = 1 (Fig. 5.11). Before the "tooth" of photo-ionization at frequencies lower than the bound of continuous absorption ν_1, are located lines of absorption. The area of all these lines (and integral of radiation is characterized namely by the area $\int \sigma_\nu\, d\nu$, if one were to digress from weighting function comparatively slowly changing with frequency) is by no means small. Really, curve of average absorption cross section near boundary of continuous absorption ν_1 continues in the direction of frequencies lower than bound in proportion to ν^{-3} (see § 11), i.e., mean cross section in region of lines is not at all small and even larger than cross section in continuum (dotted line in Fig. 5.11). Other evidence of significance of area of lines is the fact that oscillator strength for continuum of main series of an atom of hydrogen (n = 1) equals, as follows from formula (5.81), 0.49 (or, more exactly, from Table 5.4, 0.436). Thus, approximately half of oscillator strengths, and consequently also area of absorption curve, belongs to continuous spectrum, and the other half belongs to lines (sum of oscillator strengths is equal to one).

So large an area of lines is due to their colossal height, which compensates smallness of width. Let us consider, for instance, line $h\nu$ = 10 ev, which widens 100 times as compared to natural width owing to Doppler-effect. Effective cross section in the center has an order of 10^{-12} cm^2 (see formula (5.65)) which is 100 times more than the cross section of photo-ionization (see (5.34)). This signifies simply that shell of gas, optically transparent for continuous spectrum, most likely is opaque for frequencies corresponding to lines; these frequencies are "locked" in gas shell, are in thermodynamic equilibrium with substance, and their flow from surface of body is not determined by radiating ability; it does not exceed Planck flow. Role of lines powerfully compares with role of continuous spectrum only under the condition that the body will be transparent also in lines. Optical thickness of layer for continuous spectrum will become of the order of ratio of cross sections of photo-ionization and selective absorption in line, i.e., extraordinarily small, $<10^{-5}$ in given example.*

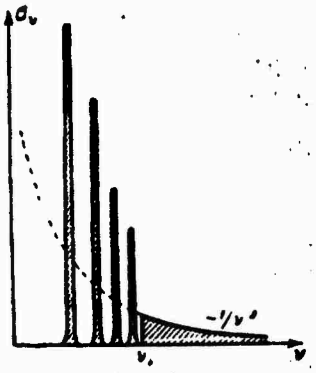

Fig. 5.11 Effective absorption cross section of light by an atom of hydrogen from ground state. Transition of discrete spectrum into continuum. Dotted line shows averaged cross section with respect to lines in region of discrete spectrum. Figure is schematic.

Regarding the Rosseland path, as one may see from Fig. 5.12, it influences not so much the area of absorption curve, but total width of lines, since owing to great magnitude of absorption in line from integral with respect to spectrum corresponding sections will be simply completely cut (range in line is practically equal to zero) independently of magnitude of absorption. Total width of lines is small as compared to total spectral interval participating in transfer.

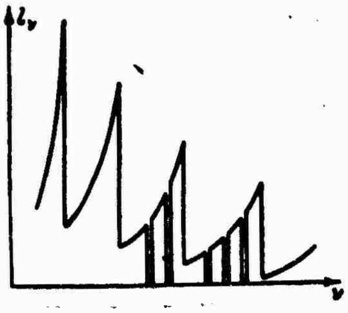

Fig. 5.12. Concerning the question of influence of lines on magnitude of path.

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*For the energy role of lines in radiation of hydrogen plasma see [49].

It is necessary to note that in gas of great density, when broadening of lines is very great, their role can become noticeable for transfer of radiant energy; the lines can noticeably lower the Rosseland path.

3. Striped Spectrum of Molecules

§ 14. Energy Levels of Diatomic Molecules

It makes sense to consider absorption of light by molecules at temperatures lower than 12,000-8,000°K, since at higher temperatures molecules completely dissociate into atoms.

The energy of an atom is determined only by its electron state. The energy of a molecule, besides the electron state, depends even on intensity of vibrational and rotational motion. Therefore, the number of energy levels and number of allowed transitions between them for molecules is much larger than for atoms; the molecular spectra is considerably more complicated than the atomic spectra. Sometimes individual lines in the spectrum are located so close to each other and their number is so big that in certain sections they form an almost continuous spectrum. At high temperatures or densities of gas due strong broadening the lines can even overlap. Therefore, striped molecular spectra of radiation and absorption in certain conditions render an essential energy influence analogous to that of continuous spectra. Molecular spectra have a large value for absorption and emission of light in air at temperatures of the order of several thousands and tens of thousands of degrees.

We will consider the simplest and at the same time the practically important case of diatomic molecules. In the first approximation electron, vibrational, and rotational motion in a molecule occur independently and total energy of the molecule can be presented in the form of the sum of corresponding components. During not too intense vibrations the latter are close to harmonious and their energy equals

$$E_{кол} = hc\omega_e\left(v+\frac{1}{2}\right), \qquad (5.86)$$

where $\omega_e = \nu_{vib}/c$ is the wave number measured in cm^{-1} (usually in spectroscopy it is accepted to use instead of frequencies ν sec^{-1} the wave numbers $\frac{1}{\lambda} = \nu/c$ cm^{-1});* $v = 0, 1, 2. . .$ is vibrational quantum number. Energy of rotation is characterized by rotary quantum number $J = 0, 1, 2, . . .$ and moment of inertia of molecule I:

$$E_{вр} = \frac{h^2 J(J+1)}{8\pi^2 I} = hcB_e J(J+1), \qquad (5.87)$$

where $B_e = h/8\pi^2 cI$ is the constant of rotation, measured in cm^{-1}.

Thus, if U_e is electron energy in a given state, then in first approximation total energy of molecule equals**

$$E = U_e + hc\omega_e\left(v+\frac{1}{2}\right) + hcB_e J(J+1). \qquad (5.88)$$

In the following approximations to expression (5.88) are added terms considering the anharmonicity of vibrations, interaction of vibrations with rotation, etc. (see [20, 41]); we will not remain on this.

Wave numbers of emitted or absorbed radiation $1/\lambda = \nu/c$ (in spectroscopy it is sometimes referred to as "frequency," measuring "frequency" in cm^{-1}) are determined by difference of energies of initial

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*To wave number 1 cm^{-1} correspond: wave length $\lambda = 10^8$ A, frequency $\nu = 3\cdot10^{10}$ sec^{-1}, energy of quantum $h\nu = 1/8060$ ev, $h\nu/k = 1.35°K$.

**Rotational energy in formulas (5.87), (5.88) is determined with an accuracy of constant depending on type of bond between rotational and electron states; on the type of bond depends also the exact meaning of rotational quantum number. The constant has the order hcB_e and it can be included in U_e, writing energy in the form of (5.88); for reference to this, see [20].

and final states. Subsequently the upper state always will be designated by one prime, and the lower by two:

$$\frac{1}{\lambda}=\frac{E'-E''}{hc}=\left[\frac{U'_e-U''_e}{hc}\right]+\left[\omega'_e\left(v'+\frac{1}{2}\right)-\omega''_e\left(v''+\frac{1}{2}\right)\right]+ \\ +[B'_eJ'(J'+1)-B''_eJ''(J''+1)]. \qquad (5.89)$$

Between differences of electron, vibrational, and rotational energies (the scale of the last two are the magnitudes $hc\omega_e$ and hcB_e) there always exists the relationship

$$\Delta E_{\text{эл}} \gg \Delta E_{\text{кол}} \gg \Delta E_{\text{вр}};\ \frac{1}{\lambda_{00}} \gg \omega_e \gg B_e, \qquad (5.90)$$

where $1/\lambda_{00} = (U'_e + \omega'_e/2 - U''_e - \omega''_e/2)/hc$ is the wave number corresponding to electron transition in absence of vibrations and rotations. In the accuracy of inequalities (5.90) one can be certain, considering Table 5.6, in which are presented spectroscopic constants of the most important states and transitions in molecules O_2, N_2, N_2^+, NO.*

The arrangement of levels of a molecule has the form shown in Fig. 5.13. The dotted line shows electron energies of levels A and B. The first actual levels of the molecule, corresponding to absence of vibrations ($v = 0$), lie somewhat higher due to zero-point energy of vibrations. To each electron state corresponds a great number of vibrational levels, and to each of the vibrational levels in turn correspond a great number of rotational levels. Vibrational levels during growth of excitation are somewhat compressed due to anharmonicity and in limit $v \to \infty$ pass into continuum, corresponding to dissociation. Rotational levels, conversely, diverge during growth of J (for not too large J numbers, when approximation (5.87)** is accurate).

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*Different electron states of a molecule differ by forms of potential curves describing interaction of atoms depending upon internuclear distance, and also mean internuclear distances (i.e., during transition from one electron state to another frequency of vibrations, moment of inertia, and constant of rotation change). The table is taken from [8].

**During very strong rotations (extraordinarily large J) change of potential curve of molecule owing to centrifugal forces becomes essential. In limit $J \to \infty$ rotational levels, just as vibrational, start to compress and pass into continuum.

Table 5.6. Spectroscopic Constants of the Most Important Molecules

Molecule	State	Electron energy U_e, ev	$h\nu_{00}=\frac{hc}{\lambda_{00}}$, ev	Transition $\frac{1}{\lambda_{00}}$, cm -1	ω_e, cm^{-1}	B_e, cm^{-1}	Transition and name of system of bands
O_2	$B^3\Sigma_u^-$	6,11	6,11	49363	700,4	0,819	$B \to X$ Schumann-Runge
	$X^3\Sigma_g^-$	0		0	1580	1,446	
N_2	$C^3\Pi_u$	11,1	3,69	29670	2035	1,826	$C \to B$. 2nd positive
	$B^3\Pi_u$	7,4	1,18	9557	1734	1,638	$B \to A$ 1st positive
	$A^3\Sigma_u^+$	6,17	6,17	49757	1460	1,440	$A \to X$ Forbidden band Vegard-Kaplan
	$X^1\Sigma_g^+$			0	2360	2,010	
NO	$B^2\Pi$	5,63	5,63	45440	1038	1,127	$B \to X$ β-band
	$A^2\Sigma^+$	5,48	5,47	44138	2371	1,995	$A \to X$ γ-band
	$X^2\Pi$			0	1904	1,705	
N_2^+	$B^2\Sigma_u^+$		3,16	25566	2420	2,083	$B \to X$ 1st negative
	$X^2\Sigma_g^+$				2207	1,932	

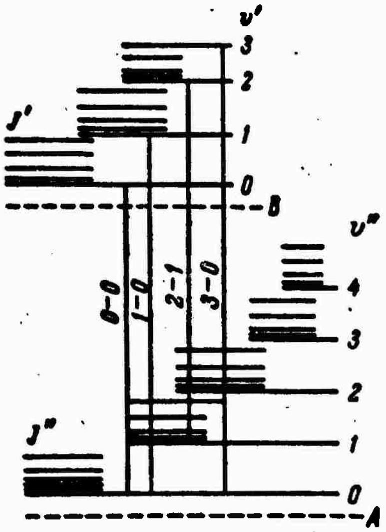

Fig. 5.13. Energy level diagram and transitions in a diatomic molecule. Vertical lines show different bands.

A diagram of levels of a molecule of nitrogen with indication of terms and their energies, and also vibrational states, is presented in Fig. 5.14. For molecules of oxygen and nitrogen oxide we present a diagram of potential curves on which are also shown terms and energy. Subsequently we frequently will have to use designations of different electron states of molecules, therefore, we will recall briefly the basic positions of spectroscopic symbolism.

An electron state is characterized by projection of orbital moment of electrons onto axis of molecule or quantum number Λ, total spin of electrons S, and properties of symmetry.

States with $\Lambda = 0, 1, 2, \ldots$ are designated by Greek letters Σ, Π, Δ, . . . Projection of spin onto axis can take 2S + 1 values, in accordance with which every term is split. Multiplicity of term 2S + 1 is indicated on the left above, for instance, ${}^3\Sigma$, ${}^2\Pi$(S = 1, S = 1/2 correspondingly).

During reflection into the plane passing through axis of molecule, projection of electron orbital moment changes sign; in conformity with this terms with orbital moment different from zero are doubly degenerated, more exact; they are split into two due to existence of interaction between rotation of molecule and motion of electrons. This phenomenon is called Λ-doubling ("lambda"-doubling).

If however $\Lambda = 0$, reflection does not at all change the electron energy; wave function is multiplied by +1 or -1. This property of symmetry Σ of terms is indicated on the upper right: Σ^+, Σ^-.

If the molecule consists of identical atoms, there appears one more property of symmetry, namely, energy is invariant relative to simultaneous change of sign of coordinates of all electrons and nuclei. The wave function is multiplied by +1 or -1, which is designated by indices g and u on the lower right, for instance Σ_g, Π_u.

As a rule, the ground state of diatomic molecules possesses full symmetry and the basic term is ${}^1\Sigma_g^+$. An exception compose is the O_2 molecule, for which the basic term is ${}^3\Sigma_g^-$, and the NO molecule with basic term ${}^2\Pi$.

Consecutive electron states are designated by letters: X (ground state), A, B, C . . . or a, b, c . . . In the case of ionized molecules a prime is added to the letters: A', b'. . . Thus, for instance, the first excitation (metastable) state of N_2 is $A^3\Sigma_u^+$.

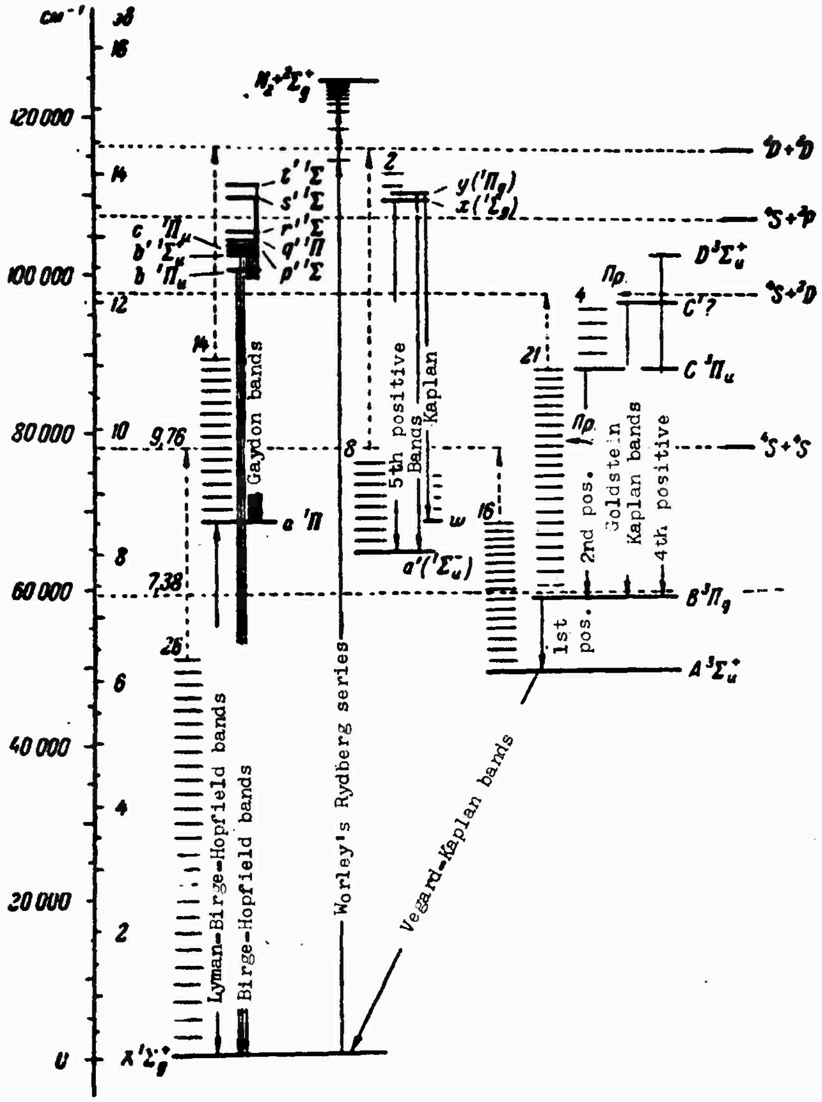

Fig. 5.14. Diagram of levels of molecule of nitrogen.

Permissible transitions between different electron states (dipole transitions with emission or absorption of light) are subordinate to certain selection rules. These rules depend on type of bond between orbital motion of electrons, their spin and rotation of molecule. In many important cases of selection the rule is the following: $\Delta\Lambda = 0 \pm 1$; multiplicity $2S + 1$ does not change; transitions $\Sigma^+ \rightleftarrows \Sigma^-$ and transitions $g \rightarrow g$, $u \rightarrow u$ are forbidden (the last two rules do not depend on type of bond)

§ 15. Structure of Molecular Spectra

Totality of transitions between two electron states B-A will form a series of bands corresponding to transitions between two given vibrational states $v'-v''$.

Frequencies of quanta radiated or absorbed during electron transitions of molecules, lie usually in ultraviolet or visible parts of the spectrum. Transitions without change of electron state correspond to frequencies belonging to infrared region of the spectrum; we will not be interested in them. Each of the bands consists of many closely located lines, corresponding to transitions between various rotational states. Rotational transitions obey selection rules, which in considerable degree simplify the spectrum. Namely, transitions are possible with the following changes of rotational quantum number: $\Delta J = J' - J'' = 0, \pm 1$, where transition 0-0 is forbidden, in the case of $\Sigma \rightarrow \Sigma$-transitions also transitions $\Delta J = 0$ are absent. In Fig. 5.13 vertical lines show transitions between different vibrational states of two electron levels (bands $v'-v''$: 0-0, 1-0, etc.). In Fig. 5.15 one band $v'-v''$ is specially separated and its rotational structure is shown. It is assumed that at least in one of the states B or A $\Lambda \neq 0$, so that $\Delta J = 0$ transitions exist. The series of lines with $\Delta J = 0, +1, -1$ are called Q-, R-, P-branches correspondingly.

If vibrational levels in different electron states were disposed with equal accuracy, i.e., frequencies ω_e' and ω_e'', would coincide, and compression due to anharmonicity would occur identically, then bands with identical value of difference $\Delta v = v' - v''$, as one may see from Fig. 5.13, would be exactly superimposed. Actually the location of levels in various electron states differ somewhat from each other, where difference of frequencies of oscillations $\omega_e' - \omega_e''$ is usually considerably less than the frequencies themselves. Therefore, bands with identical difference Δv are close to each other, forming so-called sequence of bands, whereas bands with different Δv will stand at larger frequency distances. This position is illustrated by photography of emission spectrum of so-called second positive system of nitrogen* (transition $C^3\Pi_u \rightarrow B^3\Pi_g$; see diagram of levels, Fig. 5.14). On this photography (Fig. 5.16) is scale of wave lengths and numbers of vibrational transitions are shown (first figure corresponds to upper electron state). As can be seen from photography, distance between neighboring bands of sequence Δv = -2, for instance, are equal approximately to 50 A; distance between the nearest bands of neighboring sequences is larger, for Δv = -2 and Δv = -1 it equals approximately 230 A. With increase of frequency bands compress in accordance with compression of vibrational levels when v → ∞ and finally pass into continuum, connected with dissociation

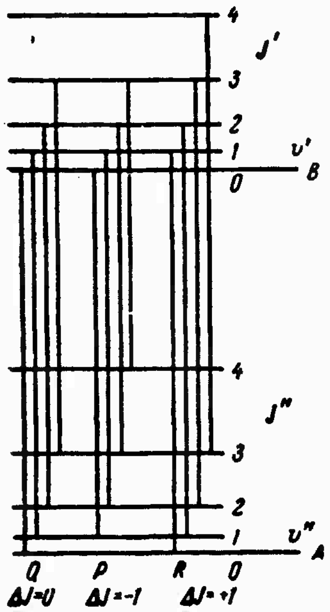

Fig. 5.15. Rotational structure of bands. Diagram of transitions corresponding to Q-, P-, and R-branches.

Fig. 5.16. Emission spectrum of second positive system of nitrogen. Photography is taken from [20a]. KEY: (a) 1 pos. group N_2; (b) 2 pos. group N_2.

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*The system of bands corresponding to different electron transitions carry usually some name. The most important systems are shown on the diagram of levels.

of molecule.

Location of lines in rotational structure of band is easy to

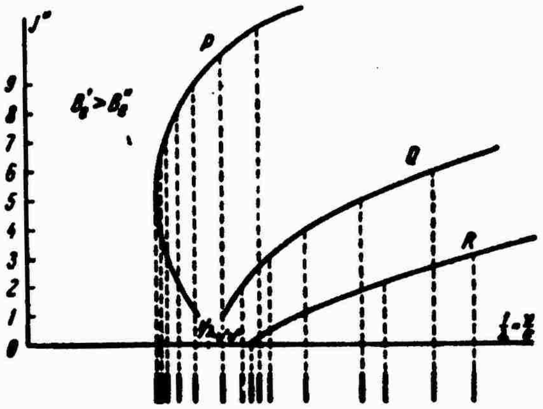

Fig. 5.17. Dependence of wave number in P-, Q- and R-branched band from rotary quantum number J" for the case $B'_e > B''_e$ (red edge).

establish, using formula (5.89) and rules of sampling: J' - J" = 0, +1, -1. We obtain for three branches the following regularities:

$$P:\ J'=J''-1,\ \frac{1}{\lambda}=\frac{1}{\lambda_{v'v''}}+(B'_e-B''_e)J''^2-(B'_e+B''_e)J'',\ J''>1; \qquad (5.90)$$

$$Q:\ J'=J'',\ \frac{1}{\lambda}=\frac{1}{\lambda_{v'v''}}+(B'_e-B''_e)J''^2+(B'_e-B''_e)J'',\ J''>1; \qquad (5.91)$$

$$R:\ J'=J''+1,\ \frac{1}{\lambda}=\frac{1}{\lambda_{v'v''}}+(B'_e-B''_e)J''^2+(3B'_e-B''_e)J''+2B'_e,\ J''>0. \qquad (5.92)$$

Here $1/\lambda_{v'v''}$ is a constant, the wave number which corresponds to electron-vibrational transition in absence of rotational structure (without third term in formula (5.89)). Rotational structure depends on which of two rotational constants is larger: B'_e or B''_e. Dependencies of wave numbers 1/λ on quantum number J" and spectrum are schematically depicted for both cases in Figs. 5.17 and 5.18 (so-called Fortra diagrams). From Fig. 5.17 it is clear that when $B'_e > B''_e$ the spectrum has a low-frequency boundary, where the lines are compressed ("red" edge); the lines spread in the direction of high frequencies and distances between them increase. When $B'_e < B''_e$, conversely, "violet" edge and lines spread in the direction of low frequencies. In region of "frequency" edge distances between lines of the order $B'_e - B''_e$ (≈ 0.2 cm^{-1} for 2nd positive system N_2 which corresponds in scale of wave lengths $\Delta\lambda \sim 0.2$ A). In region of rarefaction of lines when $J'' \gg 1$ all branches behave approximately according to the law

$$\frac{1}{\lambda} \approx \frac{1}{\lambda_{v'v''}} + (B'_e - B''_e) J''^2 \tag{5.93}$$

and distances between lines $\Delta(1/\lambda)$ grow in proportion to J".

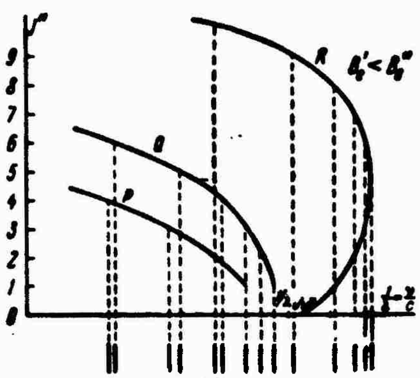

Fig. 5.18. Dependence of wave number in P-, Q- and R-branched bands on rotational quantum number J" for the case $B'_e > B''_e$ (violet edge).

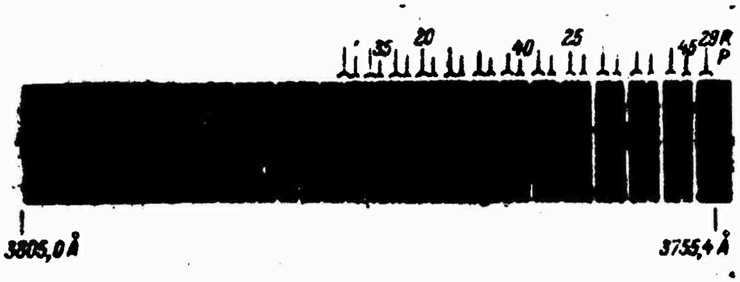

Fig. 5.19. Spectrum in band 0-2 of second positive system of nitrogen. Photography is taken from [20a].

For illustration of rotational structure we conduct photography (Fig. 5.19), on which is resolved band 0-2 of second positive system N_2. For the transition $C^3\Pi_u \rightarrow B^3\Pi_g$ of nitrogen $B'_e > B''_e$ (see Table 5.6) and the band is shaded in the "red" side ("red" edge).

Each of the lines of the rotational structure on this photography consists of three, in accordance with multiplet splitting of levels. Λ-doubling on photography is not resolved (it is usually less than 1 cm^{-1} which corresponds in scale of wave lengths when $\lambda \approx 3800$ A to $\Delta\lambda < < 1$ A).

As was already noted above, electron transitions in molecules, as also in atoms, correspond to ultraviolet or visible regions of spectrum. If the nearest unforbidden transition of their ground state into an excited state corresponds to ultraviolet quanta, the gas is transparent and is colorless, as for instance, N_2, O_2, NO. In certain molecules, such as Br_2, J_2, the nearest electron level with the allowed transition from ground state is located rather low, and the molecule absorbs visible light. Such gases are strongly colored. In the direction of large frequencies of absorption bands of molecules spread usually into the far ultraviolet region of the spectrum and pass then into a continuum.

§ 16. Franck-Condon Principle

Electron transitions in a molecule are connected with simultaneous change at once of three characteristics of its state. A great number of all possible combinations of initial and final states is limited by rules of sampling. However, selection rules are extended only to change of electron and rotational parameters of molecule and nothing refers to possible change of state of vibrations. In order to establish what combinations of vibrational quantum numbers during transitions are

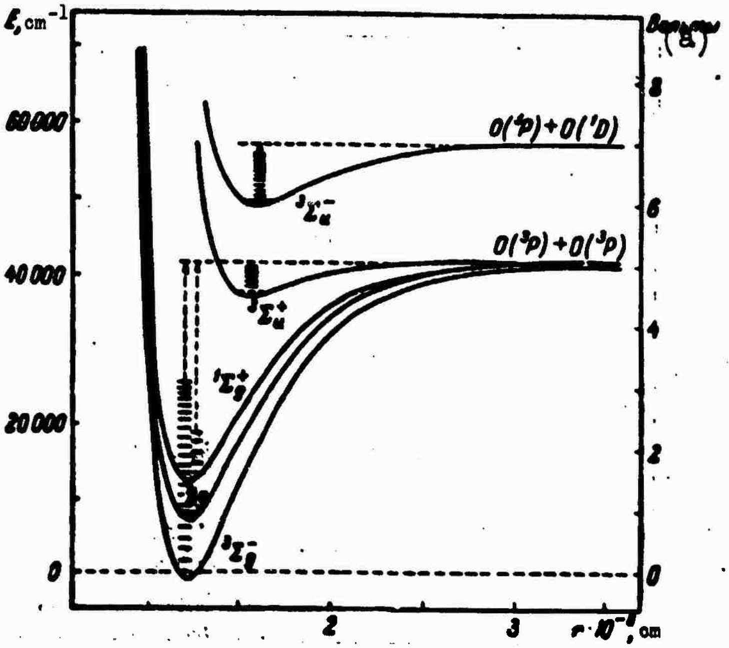

Fig. 5.20. Potential curves of an O_2 molecule.
KEY: (a) volts.

the most probable, we will turn to diagram of curves of potential energy of molecule, disregarding rotation.

Potential energy of molecule depends on internuclear distance. At approach of nuclei repulsive force predominate, during withdrawal, attractive force predominate. At certain distance r_e repulsive force and attraction forces balance one another and potential energy at this point is minimum. The absolute magnitude of minimum of potential energy corresponds to energy of electron state U_e. The difference between energy at infinite withdrawal of nuclei and this magnitude gives energy of dissociation (with an accuracy up to energy of zero vibrations). Form and position of potential curve depend on electron state, so that every molecule belongs to several curves. In Figs. 5.20 and 5.21 are shown potential curves of molecules of O_2 and NO, built on the basis of spectroscopic data.* On the figures are drawn horizontal lines, corresponding to levels of oscillatory energy in each of the electron states.

From the classical point of view the internuclear distance at a given energy of vibrations periodically changes near position of equilibrium r_e. The change occurs in the interval between points in which the horizontal line corresponding to energy of vibrations, intersects the potential curve. In intersection points speed of relative motion of nuclei turns into zero, since direction of motion changes and in these positions (points of return) the molecule remains longest of all. Conversely, it goes past the position of equilibrium very rapidly, since speed here is maximum.

Therefore, spontaneous transition from upper electron state into lower most frequently occurs when nuclei occupy extreme positions. Reconstruction of electron shell during transition with emission of quantum occurs so fast that during that time neither position of nuclei

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*Figures are taken from [20, 21].

nor their kinetic energies can change. Really, duration of reconstruction is measured by the time during which electron passes a distance of the order of dimensions of molecule, i.e., $\sim 10^{-16}$ sec (when velocity of an electron $\sim 10^{8}$ cm/sec and dimensions of molecule $\sim 10^{-8}$ cm). Distance between nuclei noticeably changes during the time of order of period of vibrations, i.e., during the time $\sim 1/\omega_e c \sim 10^{-14}$ sec (when $\omega_e \sim 1000$ cm^{-1}, which pertains to light molecules; in heavy molecules ω_e is still less, and the period of vibrations is larger.*

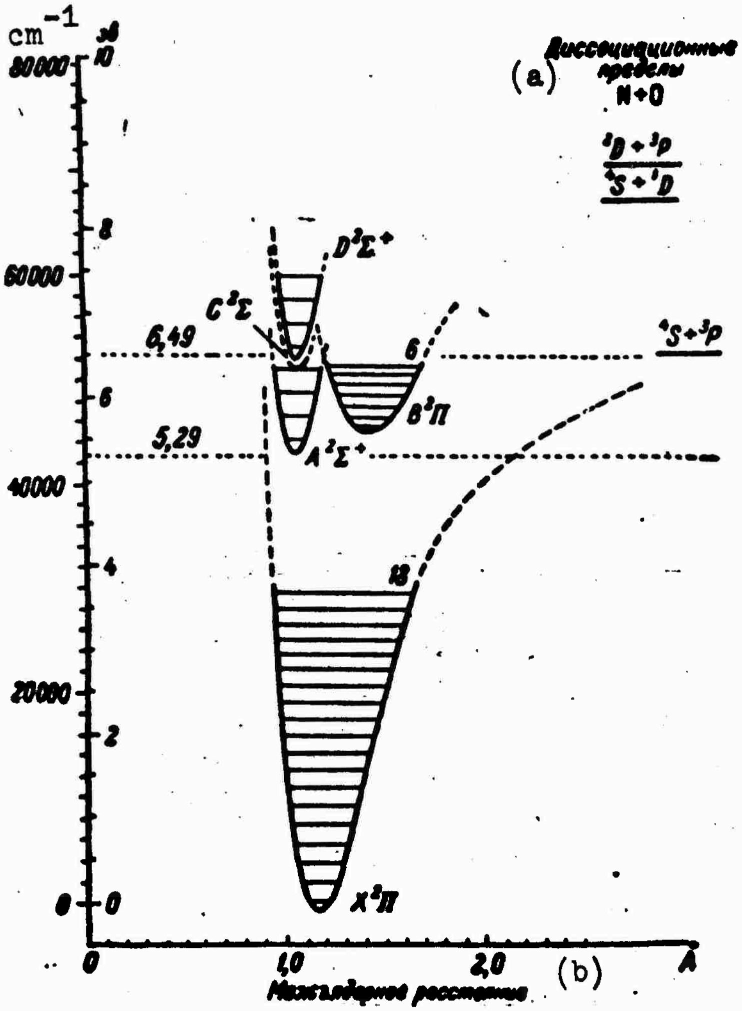

Fig. 5.21. Potential curves of NO molecule. KEY: (a) dissociation range; (b) internuclear distances.

Electron transition into lower state is accomplished at a constant internuclear distance, i.e., mainly along verticals conducted from points of return on diagram of potential curves (Fig. 5.22).

In final state molecule arrives with zero velocity i.e., starts

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*Probability of unforbidden electron transitions from upper state into lower state in atoms and molecules is of the order of 10^{8} sec^{-1}. Thus, an excited molecule during a time of the order of 10^{-8} sec (for which atoms accomplish much, $\sim 10^{6}$ vibrations) is in upper state, but then during the time $\sim 10^{-16}$ sec it transfers into the lower state, emitting light quantum.

vibrational motion with new vibrational energy also from points of return.

Thus, the easiest transitions of all are accomplished into such lower vibrational states for which one of the points of return is located on the same internuclear distance as one of the points of return in the upper state. This position, known under the name of the principle of Frank-Condon, is illustrated by Fig. 5.22, on which are verticals of the most probable transitions of their upper state v' = 4 into lower v" = 0 and v" = 6.

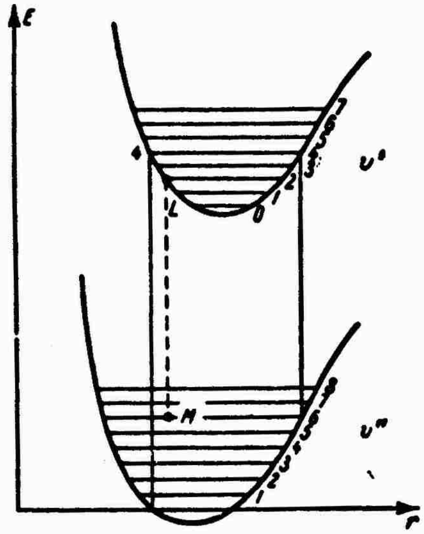

Fig. 5.22. Diagram of potential curves and transitions, illustrating Franck-Condon principle.

Conversely, transitions for which verticals from peaks of return fall in the middle of segment of the lower level or in general, go beyond the limits of the segment limited by the potential curve (as, for instance, transition 2-6, shown in Fig. 5.22 by the dotted line), are doubtful.

§ 17. Probabilities of Molecular Transitions with Emission of Light

Let us consider transition of molecule from upper state into lower state from the quantum-mechanical point of view.

The probability of a spontaneous dipole transition with emission of light quantum is proportional to the square of matrix element of dipole moment of system **d** and is described by general formula (5.69). Let us consider the transition from upper state Bv'J'M' into lower state Av"J"M". Indices B and A designate electron states of molecule; v', v" are vibrational states, and J', J" are rotational quantum numbers. M is "magnetic" quantum number determining magnitude of projection of rotational moment onto axis of molecule. It can take 2J + 1 values: M = J, J - 1, . . ., - J. Rotational energy does not depend on it, and wave function of system Ψ does depend. Matrix element equals

$$D_{Av''J''M''}^{Bv'J'M'} = \int \Psi^{*}_{Bv'J'M'}\, \mathbf{d}\, \Psi_{Av''J''M''}\, d\tau, \tag{5.94}$$

where integration is produced with respect to all coordinates on which wave function of system depends.

We will as before originate from simplified model of molecule, in which motion of electrons, vibration, and rotation are assumed to be not dependent on each other. The full wave function can be presented in the form of the product of three wave functions Ψ_{el}, Ψ_{vib}, Ψ_{rot}, describing electrons, vibrational motion and rotational motion. They depend on corresponding coordinates: Ψ_{el} on coordinates of electrons, Ψ_{vib} on internuclear distance, Ψ_{rot} on angles of turn of molecule, and also on corresponding quantum numbers. For instance, for upper state:

$$\Psi_{Bv'J'M'} = \psi_{\text{эл}\,B}\, \psi_{\text{кол}\,v',\,B}\, \psi_{\text{вр}\,J',\,M'}. \tag{5.95}$$

Ψ_{vib} depends on electron state, since frequency of vibrations depend on the latter.

Let us present dipole moment of system $\mathbf{d} = \Sigma e_i \mathbf{r}_i$ (sum is extended to all particles) in the form of sum of electron and nuclear moments $\mathbf{d} = \mathbf{d}_e + \mathbf{d}_a$. Electron wave functions, by definition, are orthogonal in different electron states (nuclear coordinates enter into them only as parameters). Upon substitution of **d** and Ψ into integral (5.95) in the term with nuclear moment is eliminated factor $\int \psi^{*}_{el\,B}\, \psi_{el\,A}\, d\tau_{el}$, which turns into zero when B ≠ A, so that matrix element disappears from nuclear moment. Inasmuch as Ψ_{vib} and Ψ_{rot} do not depend on coordinates of electrons, the remaining matrix element from electron moment can be presented in the form of product:

$$D = D_e = \int \psi^*_{\text{эл}} | d_e | \psi_{\text{эл}} \int \psi^*_{\text{кол}} \psi_{\text{кол}} \cdot \int \psi^*_{\text{вр}} n \psi_{\text{вр}} = D_{\text{эл}} \cdot D_{\text{кол}} \cdot D_{\text{вр}}, \tag{5.96}$$

where in rotational matrix element entered only direction of averaged electron dipole moment — unit vector **n**, which is averaged with respect to "turns" of molecule. (For brevity we omitted here indices — quantum numbers for wave functions and differentials). The condition that D_{rot} be different than zero also gives selection rule for change of rotational quantum numbers during transition.

Energy of molecule in our approximation does not depend on direction of rotational moment; therefore, in order to obtain probability of transition from one energy state, Bv'J', into another, Av"J", probability must be averaged with respect to all possible directions of rotational moment in initial state and summed over directions in the final state. Thus, probability of transition in units $\sec^{-1}$ according to (5.69) equals:*

$$A^{Bv'J'}_{Av''J''} = \frac{64\pi^4}{3hc^3} \nu^3_{Bv'J',\,Av''J''} D^2_{\text{эл}\,BA} q_{v'v''} p_{J'J''}, \tag{5.97}$$

where

$$q_{v'v''} = D^2_{\text{кол}\,v'v''} = \left| \int \psi^*_{\text{кол}\,v'}(r)\, \psi_{\text{кол}\,v''}(r)\, dr \right|^2, \tag{5.98}$$

$$p_{J'J''} = \frac{1}{2J'+1} \sum_{M'M''} D^2_{\text{вр}\,J'M',\,J''M''}. \tag{5.99}$$

Intensity of corresponding line in spectrum in erg/cm^3·sec equals the product of probability of transition A(1/sec), energy of quantum

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*Strictly speaking, electron matrix element D_{el} depends on internuclear distance r (it is calculated in a specific moment of time, at fixed internuclear distance which enters into electron wave functions). By magnitude D^2_{el}, which enters in formula for probability of transition (5.97), one should imply certain value D^2_{el} average with respect to r, let us say, corresponding to position of equilibrium r_e in upper electron state.

$h\nu$(erg) and number of molecules N(1/cm^3) remaining in upper quantum state: I = $h\nu$NA (for brevity indices are emitted).

Dimensionless probability $p_{J'J''}$ determines distribution of intensity in lines of rotational structure inside given band Bv' → Av". In quantum mechanics of molecule it is proved that $p_{J'J''}$ obeys rule of sums:

$$\sum_{J''} p_{J'J''} = \sum_{J''} \sum_{M'M''} \frac{1}{2J'+1} D^2_{\text{эл}J'M',J''M''} = 1, \tag{5.100}$$

whose meaning is that during the accomplished transition from upper electron vibrational state into lower state the molecule must fall on one of the possible rotational levels J" (corresponding probability is equal to one).

Probability of transition Bv' → Av" to any of the rotational levels is obtained by means of summation of expression (5.97) over J". In accordance with condition (5.100), it equals

$$A^{Bv'}_{Av''} = \frac{64\pi^4}{3hc^3} \nu^3_{Bv',Av''} D^2_{\text{эл}BA} q_{v'v''}, \tag{5.101}$$

where $\nu_{Bv', Av''}$ is certain average frequency for given band (in virtue of smallness of rotational energies as compared to vibrational energies, the scattering of frequencies inside the band is small and introduction of average frequency for the band is justified).

Relative probability of vibrational transformation v' → v" during electron transition B → A is characterized by dimensionless factor $q_{v'v''}$, determined by formula (5.98).

Let us consider integral (5.98). Wave functions belong to different electron states, i.e., differ by frequency of vibrations and position of equilibrium r_c. Owing to this the integral is different than zero for different v'v" combinations, and for vibrations there are no rules of sampling (if electron state did not change and vibration would be strictly harmonic, integral (5.98) in virtue of condition of orthogonality would be equal to zero for all $v' \neq v''$).

Wave functions of different vibrational states are schematically depicted in Fig. 5.23. So that integral (5.98) from product of vibrational factors (does not vibrate only $\Psi_{vib,\ v\,=\,0}$) has considerable magnitude, it is necessary that, first, factors not be in "reversed phase" and, secondly, that high maxima of both factors overlap. But the largest maxima of vibrational wave functions lie in "cusps," which also indicates the biggest probability of these positions. Therefore those transitions are most probable for which at least one point of return in upper state is on the same internuclear distance as the point of return in the lower state. The given reasoning substantiates the principle of Frank — Condon from the quantum-mechanical point of view. Magnitude $q_{v'v''}$, called frequently the Frank — Condon factor, is the probability of given vibrational transition $v' \rightarrow v''$ during the electron transition which takes place, since by the rule of sums for matrix elements total probability of transition from given v' into any v'' is equal to one:

$$\sum_{v''} q_{v'v''} = \sum_{v''} D^2_{\text{KCH}\ v'v''} = 1. \tag{5.102}$$

To illustrate the presented quantum-mechanical interpretation of the principle of Frank — Condon we presented in [21] a table of integrals $|\int \psi^*_{v'} \psi^*_{v''}\, dr|$, the square of which equals $q_{v'v''}$ for β-system $NO(B^2\Pi \rightarrow X^2\Pi)$. It is useful to consider Table 5.7 simultaneously with the diagram of potential curves Fig. 5.21, checking, thus, fulfillment of Frank — Condon principle.

A knowledge of Frank — Condon factors is necessary for calculation of relative probabilities of different $v' \rightarrow v''$ transitions, i.e., relative intensities of different bands in the framework of given electron transition. They are calculated for a number of systems of the most important molecules: NO, O_2, N_2, N_2^+ (see [8, 21-24]).

In order to find absolute values of probabilities of transitions and intensities of lines or bands, it is necessary to know the value of electron matrix element D_{el}. Theoretical calculation of electron matrix element D_{el} is very difficult. Usually it is found from experiment (see §§ 18 and 21). By analogy with the theory of atomic transitions, instead of electron matrix element the idea of oscillator strength is usually used.

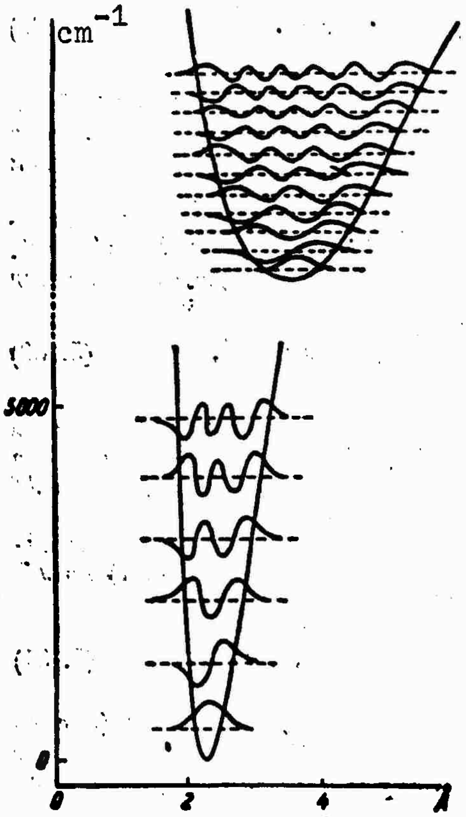

Fig. 5.23. Potential curves and wave functions of a series of vibrational states for a RbH molecule. (graph is taken from [20b]). The number of zeroes (nodes) for every wave function is equal to vibrational quantum number v.

Let us sum probability of transition $A_{Bv' \rightarrow Av''}$ according to formula (5.101) over final vibrational states v" and average with respect to initial v'. Let us obtain probability of electron transition B → A during arbitrary vibrational and rotational transformations:

$$A_{BA}=\frac{64\pi^4}{3hc^3}\nu_{BA}^3 D^2_{\text{эл}\,BA}, \tag{5.103}$$

where ν_{BA} is a certain average frequency for electron transition (just as earlier, justification for introduction of average frequency was the fact that differences of vibrational energies are small as compared to difference of electron energies). Using formulas (5.69), (5.73), (5.60), we will determine oscillator strength for electron transition B → A:

$$f_{BA}=\frac{8\pi^2 m}{3he^2}\nu_{BA}D^2_{v\pi\, BA}. \qquad (5.104)$$

Table 5.7. Square Root from Frank — Condon Factor $\sqrt{q_{v'v''}}$ for β-system of Bands of NO molecule (v' Pertains to Upper State, v" - to Lower)*

v"	Vibrational quantum number of upper state v'								
	0	1	2	3	4	5	6	7	8
0	0,0000	0,0002	0,0010	0,0032	0,0079	0,0161	0,0280	0,0429	0,0587
1	0,0003	0,0024	0,0087	0,0219	0,0414	0,0625	0,0788	0,0811	0,0707
2	0,0021	0,0119	0,0336	0,0619	0,0819	0,0803	0,0569	0,0257	0,0040
3	0,0086	0,0364	0,0735	0,0896	0,0680	0,0273	0,0016	0,0065	0,0286
4	0,0250	0,0750	0,0967	0,0607	0,0115	0,0025	0,0286	0,0471	0,0362
5	0,0554	0,1069	0,0693	0,0077	0,0100	0,0447	0,0448	0,0146	0,0001
6	0,0972	0,1020	0,0153	0,0121	0,0530	0,0371	0,0027	0,0097	0,0341
7	0,1380	0,0556	0,0041	0,0573	0,0363	0,0001	0,0231	0,0401	0,0170
8	0,1603	0,0075	0,0497	0,0489	0,0000	0,0317	0,0389	0,0055	0,0066
9	0,1522	0,0101	0,0756	0,0046	0,0629	0,0004	0,0567		
10	0,1276	0,0452	0,0391	0,0395	0,0286	0,0301	0,0299		
11	0,0964	0,0849	0,0059	0,0686	0,0006	0,0572	0,0003		
12	0,0657	0,1100	0,0033	0,0599	0,0158	0,0382	0,0198		
13	0,0405	0,1123	0,0318	0,0252	0,0515	0,0047	0,0506		
14	0,0226	0,0956	0,0704	0,0010	0,0619	0,0070	0,0399		
15	0,0113	0,0698	0,0962	0,0102	0,0363	0,0404	0,0070		
16	0,0051	0,0442	0,0985	0,0449	0,0057	0,0587	0,0046		
17	0,0021	0,0246	0,0816	0,0793	0,0036	0,0394	0,0361		
18	0,0007	0,0120	0,0565	0,0932	0,0329	0,0080	0,0557		
19	0,0002	0,0051	0,0334	0,0838	0,0693	0,0022	0,0374		
20	0,0001	0,0019	0,0169	0,0610	0,0881	0,0297	0,0068		
21		0,0006	0,0074	0,0369	0,0821	0,0663	0,0031		
22		0,0002	0,0028	0,0188	0,0603	0,0852	0,0326		
23			0,0009	0,0801	0,0361	0,0784	0,0685		
24				0,0030	0,0179	0,0559	0,0865		
25				0,0009	0,0074	0,0331	0,0727		
26					0,0026	0,0150	0,0486		
27					0,0007	0,0057	0,0258		
28						0,0018	0,0110		
29							0,0038		
	$v'=9$	10	11	12	13	14	15	16	17
	$v''=0$; 0,0731	0,0837	0,0892	0,0866	0,0841	0,0744	0,0601	0,0445	0,0303
	$v'=18$	19	20	21	22	23	24	25	26
	$v''=0$; 0,0190	0,0110	0,0059	0,0029	0,0013	0,0006	0,0002	0,0001	0,0000

*Rectangles — the most probable transitions from every upper state.

The ratio of statistical scales of upper and lower electron states here is taken equal to one on the assumption that multiplicities of both terms are identical. It is necessary to expect that oscillator strengths for molecular transitions have the same order as those for atomic transitions. Numerical values of oscillator strengths for the most important systems will be given below.

§ 18. Coefficient of Absorption of Light in Lines

To calculate line absorption coefficient corresponding to transition $Av''J'' \rightarrow Bv'J'$, which is the converse with respect to transition with emission of light of that considered in the preceding paragraph, we will use the principle of detailed balancing. The latter establishes a connection between coefficients of Einstein for direct and reverse transitions (5.71).* Substituting in this relationship the emission probability according to formula (5.97), taking into account determination (5.70) and replacing in expression (5.97) D_{el}^2 by oscillator strength according to formula (5.104), we will obtain coefficient of absorption in the form

$$\varkappa_{Av''J'',\,Bv'J'} = \frac{\pi e^2}{mc} f_{BA} q_{v''v'} p_{J''J'} N_{Av''J''} F(\nu), \qquad (5.105)$$

where $N_{Av''J''}$ is the number of molecules in 1 cm^3, being in lower state $Av''J''$, and $F(\nu)$ is the function describing distribution of absorption inside line; it is standardized per unit $\int F(\nu)\,d\nu = 1$.

We will integrate the coefficient of absorption connected with electron transition $A \rightarrow B$, over the whole spectrum. Obviously, the same result will be obtained if we will integrate over frequency the coefficient of absorption of every line (5.105) and will sum over all lines of the spectrum.** Summation over lines is equivalent to

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*The ratio of statistical weights in this formula, as also before, is considered equal to one. See (5.104).

**Here one should include also the continuum which starts from that frequency at which bands converge to limit of dissociation.

summation over all initial and final v"J", v'J' states. Summation over final states is carried out with help of rules of sums (5.100), (5.102); summation over initial states is brought to summation over numbers of molecules; $N_A = \sum_{v''J''} N_{Av''J''}$, where N_A is the number of molecules in 1 cm^3 which is in electron state A. If A is ground state, then N_A for practical purposes equals total number of molecules in 1 cm^3 N.

For integral over spectrum from effective absorption cross section of molecule in state A during transition of it into state B $\sigma_\nu = \varkappa_\nu / N_A$, we will obtain

$$\int_0^\infty \sigma_\nu \, d\nu = \frac{\pi e^2}{mc} f_{BA}. \qquad (5.106)$$

This relationship is in full conformity with the same relationship for atomic transitions. Thus, as in the case of atoms, "area" of absorption corresponding to given electron transition, is determined only by oscillator strength. The difference is that in molecules this "area" is distributed with respect to very many lines, owing to which on each of the lines is only a small part of it. Accordingly the "height" of the molecular lines is much less than the "height" of the atomic lines. Multiplet splitting of lines and Λ-doubling still lower the "height" of lines a few times, not changing total "area."

By means of experimental investigation of absorption spectrum of molecules one can determine oscillator strength for a given system of bands. With this purpose is measured weakening of light by an optical film of gas, transparent in peaks of lines. This permits finding "area" of absorption spectrum and calculation of oscillator strength by formula (5.106). If Frank – Condon factor is known from calculation, then for estimate of oscillator strength it is possible to directly use absorption curve in separate line or band (for probabilities of rotational transitions $p_{J''J'}$ there exist simple formulas).

In such a way, for instance in [25] oscillator strengths were measured for γ- and β-bands of a NO molecule (γ: $X^2\Pi \rightarrow A^2\Sigma^+$; β: $X^2\Pi \rightarrow B^2\Pi$). It turned out that $f_\gamma \approx 0.0025$, $f_\beta \approx 0.008$. In [26] oscillator strength was found for system of Schumann — Runge bands of a molecule of oxygen (transition $X^3\Sigma_g^- \rightarrow B^3\Sigma_u^-$): $f = 0.259$, while of the total "area" of absorption bands occupy the fraction $\Delta f = 0.044$ and continuum occupies fraction $\Delta f = 0.215$, corresponding to dissociation of O_2 molecules into $O(^3P) + O(^1D)$ atoms. The continuum starts when $\lambda = 1760$ A (lower bound of bands $\lambda = 2030$ A). The effective cross section in the continuum has a maximum when $\lambda = 1450$ A, equal $\sigma_\nu = 1.81 \cdot 10^{-17}$ cm^2, and drops in half to $\lambda = 1567$ A and $\lambda = 1370$ A. It is necessary to note that value of oscillator strength for Schumann — Runge bands, extracted from data on radiation of light at high temperatures, turns out to be much less (see § 20; in [26] absorption of light by cold oxygen was measured). In connection with possible causes of such a difference, see [27].

In general, one should note that, in distinction from atomic transitions, the oscillator strength for molecular transition is not strictly constant (in particular, it depends on degree of vibrational excitation and method of averaging with respect to internuclear distance). Source materials about oscillator strength for the same transitions frequently strongly differ. A summary of known results on oscillator strengths for molecular transitions and references to literature can be found in the survey of V. N. Soshnikov [27a].

§ 19. Molecular Absorption at High Temperatures

At room temperature practically all molecules are in the ground electron and vibrational states. Thus, for instance, in a portion $\sim 10^{-5}$ molecules of nitrogen only one vibrational quantum is excited.

Long-wave boundary of absorption of diatomic molecules lies always in ultraviolet or visible regions of spectrum: for instance, for O_2, NO, N_2 molecules it is in the far ultraviolet region,* for molecules of Br_2, J_2, CN it is in the visible region. With an increase of temperature in the gas appear excited molecules, which are in the upper vibrational states, from which transition into that same upper electron state requires energy. Thus, with increase of temperature long-wave boundary of absorption shifts to the "red" side. At temperatures of the order of 10,000 degrees molecules in upper electron states appear also, from which new transitions into still higher electron states are possible; so appears absorption in first and second positive systems of nitrogen (transitions $A^3\Sigma_u \rightarrow B^3\Pi_g$ and $B^3\Pi_g \rightarrow C^3\Pi_u$; see Table 5.6 and Fig. 5.14.

Let us consider molecular absorption of light at high temperatures in the example of molecules of NO. Nitrogen oxide will be formed in air at temperatures of the order of 2,000-10,000 degrees K in rather considerable concentration of the order of several percent (see § 4 Ch. III). Absorption of light by NO molecules, as one will see later, in certain conditions plays an essential role for optical properties of heated air. Calculations of absorption by NO molecules were made in [21], which we will basically follow.

There are three important systems of NO absorption bands from the ground electron state: γ (transition $X^2\Pi \rightarrow A^2\Sigma^+$), β ($X^2\Pi \rightarrow B^2\Pi$) and δ ($X^2\Pi \rightarrow C^3\Sigma$). Long-wave boundaries of the first two systems correspond to $\sim$45,000 cm^{-1}, of the third $\sim$52,000 cm^{-1} (see Table 5.6). In absorption of light at temperatures T $\sim$3,000-10,000°K a basic

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*Transitions to low-lying levels ${}^1\Delta_g$ and ${}^1\Sigma_g^+$ in an O_2 molecule are forbidden. Also forbidden is transition to the level ${}^3\Sigma_u^+$. Corresponding to the latter Herzberg bands are extraordinarily weak. Transition $X^1\Sigma \rightarrow A^3\Sigma_u$ in N_2 (Vegard — Kaplan bands are very weak) is also forbidden.

role is played by the β-system, since by the principle of Frank — Condon probable transitions in γ- and δ-systems occur without a large change of the vibration number, i.e., basically high frequencies are absorbed of the order of 45,000-52,000 cm^{-1}, which lie in far ultraviolet region and are not so essential with such temperatures. Conversely, in β-system transitions are probable from high lower vibration states with $v'' \sim 12$ to the ground upper state $v' \sim 0$, which give an absorption in close ultraviolet and visible regions of spectrum ~25,000 cm^{-1}.

With large densities of gas and high temperatures molecular lines strongly widen and can even overlap. Here the spectrum becomes almost continuous.

Let us compare width of lines and average distance between them for a NO β-system. In estimating we will assume that temperature $T = 8{,}000^\circ$K and density of gas is equal to normal air density.

At a temperature of $8{,}000^\circ$K the Doppler width of lines with frequencies ~25,000 cm^{-1} has the order of 0.3 cm^{-1}. If one were to assume that every gas kinetic collision changes state of vibrational or rotational motion, then broadening due to collisions turns out to be large, of the order

$$\frac{\Delta\nu}{c} = \frac{N\sigma_{\text{газ}}\bar{v}}{2\pi c} \approx \frac{3\cdot10^{19}\cdot5\cdot10^{-15}\cdot1{,}5\cdot10^{6}}{2\pi\cdot3\cdot10^{10}} \approx 1{,}2\ \text{cm}^{-1}.$$

Let us estimate average distance between β lines of NO system in frequency interval from 15,000 cm^{-1} to 45,000 cm^{-1}. For absorption at least quantum 15,000 cm^{-1} the molecule should be excited to an energy of 45,000-15,000 = 30,000 cm^{-1}, i.e., to a vibrational level of $v'' \approx 20$. Considering the diagram of potential curves and considering Frank — Condon principle, it may be concluded that from every lower vibrational level transitions are probable approximately in five upper states, i.e., the considered interval contains in itself approximately $20 \cdot 5 = 100$ bands. At temperature $T = 8{,}000^{\circ}$K rotational excitation to 2-3 kT is essential, which corresponds to 7,500 cm^{-1}, i.e., in the transitions there take part approximately $J'' \approx \sqrt{2.5\ kT/hcB_e} \approx 80$ rotational levels of the lower state. Each of them gives two lines: $J' = J'' + 1$ and $J' = J'' - 1$ (Q-branch $J' = J''$ is usually very weak when $J'' \gtrsim 10$), i.e., there are in all 160 rotational lines in a band. Each of them is doubled due to multiplet splitting and once again is split into two due to Λ-doubling. Thus, in the considered frequency interval 30,000 cm^{-1} there are approximately $100 \cdot 160 \cdot 2 \cdot 2 = 64{,}000$ lines. The average distance between them is of the order 0.5 cm^{-1}; inasmuch as the width of lines ~ 1 cm^{-1}, the lines strongly overlap and the spectrum indeed is almost continuous.

Let us estimate coefficient of absorption in a rough approximation. During average vibrational excitation of a molecule of the order kT, i.e., an order of 5,000 cm^{-1} when $T = 8{,}000^{\circ}$K, the most probable transitions are to low vibrational levels of an upper state. Let us assume for estimation that light is absorbed basically during transitions to the level $v' = 0$ of an upper electron state. Then quantum $h\nu$ are absorbed only by molecules excited to energy $E_0 - h\nu$, where E_0 is energy of upper electron state. The number of such molecules according to the law of Boltzmann is proportional to $\exp\left(-\frac{E_0 - h\nu}{kT}\right)$. Let us present coefficient of absorption in the form of (5.82), expressing absorption cross section by differential oscillator strength

$$\varkappa_\nu = \frac{\pi e^2}{mc} N \frac{df}{d\nu},$$

where N is the number of NO molecules in 1 cm^3. Taking into account that by the Frank — Condon principle the probability of absorption of quanta exceeding E_0 is very small, one may assume that the whole "area" of absorption $\int\limits_{0}^{\infty}(df/d\nu)\,d\nu$ is concentrated basically in the interval of frequencies from 0 to E_0/h and contribution in integral of region ν from E_0/h to ∞ is very small. Considering that $\varkappa_\nu \sim \frac{df}{d\nu} \sim$ $\sim \exp\left(-\frac{E_0-h\nu}{kT}\right)$, we will find proportionality factor from condition (5.106) or, which is the same, from the condition of equality of integral $\int\limits_{0}^{E_0/h}(df/d\nu)\,d\nu$ to oscillator strength f. Let us obtain, thus, that

$$\frac{df}{d\nu}=f\frac{h}{kT}\exp\left(-\frac{E_0-h\nu}{kT}\right)$$

and

$$\varkappa_\nu=\frac{\pi e^2}{mc}fN\frac{h}{kT}e^{-\frac{E_0-h\nu}{kT}}. \qquad (5.107)$$

Let us introduce instead of N the number of NO molecules in 1 cm^3, their concentration in air $c_{NO} = N\rho_0/N_0\rho$, where N_0 is the number of molecules in 1 cm^3 of air under normal conditions, and ρ/ρ_0 is the ratio of air density to normal – $\rho_0 = 1.27 \cdot 10^{-3}$ g/cm^3. Let us cross from frequencies of light to wave numbers $1/\lambda = \nu/c$.

We will obtain:

$$\varkappa_\lambda=\frac{3.4\cdot 10^7}{T^\circ}f\cdot c_{NO}\frac{\rho}{\rho_0}e^{-\frac{1.44}{T^\circ}\left(\frac{1}{\lambda_{00}}-\frac{1}{\lambda}\right)}\ cm^{-1}. \qquad (5.108)$$

Here $1/\lambda_{00} = E_0/hc$ (this magnitude equals for β-system NO 45440 cm^{-1}). In formula (5.108) $1/\lambda_{00}$ and $1/\lambda$ are expressed in 1 cm^{-1}. Knowing oscillator strength, it is possible, consequently, to estimate coefficient of absorption. Considering for β-system of NO $f_\beta \approx 0.006$ (see § 20), we will find for red light $\lambda = 6500$ A when $\rho/\rho_0 = 1$, $T = 8{,}000^\circ K$ ($c_{NO} = 0.036$), $\varkappa_{NO} \approx 4.1 \cdot 10^{-3}$ cm^{-1} (effective cross section on molecule $\sigma_{NO} = \varkappa_{NO}/N_{NO} = 4.3 \cdot 10^{-21}$ cm^2).

With respect to location of potential curves and fulfillment of Frank – Condon principle transitions in basic system of absorption of oxygen O_2 (Schumann – Runge system) are fully analogous to β-system of NO, so that for estimation of coefficient of absorption of O_2 at high temperatures it is also possible to use formulas (5.107), (5.108), in which one should, of course, put the constant for O_2.

§ 20. Definitized Calculation of Coefficient of Molecular Absorption at High Temperatures

For more exact calculations (see [8, 21, 28]) it is necessary to originate from strict formula for line absorption coefficient and to consider actual probability of vibrational transitions. We will as before consider that lines are so expanded that they almost (or noticeably) overlap.

Let us introduce into consideration average coefficient of absorption of frequency ν for given electron transition A → B, averaging the true coefficient in small spectral interval from ν to $\nu + \Delta\nu$, as was done in § 12. For this it is necessary to integrate coefficient of absorption for separate line (5.105) with respect to frequency (here we will obtain "area" of one line) and to sum integral over all lines contained in interval of frequencies from ν to $\nu + \Delta\nu$. The obtained result will equal $\bar{\varkappa}_\nu \Delta\nu$. Performing this operation just as during derivation of formula (5.106), we will find averaged coefficient of absorption of frequency ν for given electron transition,

$$\bar{\varkappa}_{\nu_{AB}} = \frac{\pi e^2}{mc} \frac{f_{BA}}{\Delta\nu} \sum_{\text{bands}} q_{v''v'} \sum_{J''} N_{Av''J''}. \tag{5.109}$$

Sums over J" and over bands are extended to those initial rotational levels and those bands which give lines falling in the considered spectral section $\Delta\nu$. The number of molecules in state $A_{v''}J''$ at a temperature T can be calculated by the formula of Boltzmann, putting in it the energy of a molecule in given vibrational and rotational states (see [29]):

$$N_{Av''J''}=N_A\frac{e^{-\frac{hc\omega_A v''}{kT}}}{Z_{vA}}\frac{(2J''+1)e^{-\frac{hcB_AJ''(J''+1)}{kT}}}{Z_{rA}}. \tag{5.110}$$

Here N_A is the number of molecules in electron state A;

$$Z_{vA}=\left(1-e^{-\frac{hc\omega_A}{kT}}\right)^{-1}\approx\frac{kT}{hc\omega_A}\text{ and }Z_{rA}=\frac{kT}{hcB_A}$$

— vibrational and rotational statistical sums in lower electron state.

Basically the band will be filled by lines with large rotational numbers $J'' \gg 1$, for which, according to formulas (5.90), (5.91), it is possible to set approximately wave numbers equal to

$$\frac{1}{\lambda}=\frac{1}{\lambda_{v''v'}}+(B_B-B_A)J''^2. \tag{5.111}$$

Interval of frequencies $\Delta\nu$ fill line of band $v''v'$, corresponding to rotational numbers from J'' to $J''+\Delta J''$, where $\Delta J''$ is determined by differentiation (5.111):

$$\frac{\Delta\nu}{c}=\Delta\left(\frac{1}{\lambda}\right)=(B_B-B_A)2J''\Delta J''. \tag{5.112}$$

Assuming that $J'' \gg 1$, $\Delta J'' \ll J''$ (interval $\Delta\nu$ is sufficiently small), it is possible to consider all $\Delta J''$ of terms in the sum over J'' in formula (5.109) as the same. Ignoring units in comparison with J'', we will place in index of exponential of formula (5.110) J''^2 according to formula (5.111) and will replace $\Delta\nu$ in formula (5.109) by expression (5.112). Removing in formula (5.109) the exponential factor, in order to bring final expression into conformity with approximate formula (5.107), we will obtain

$$\bar{\varkappa}_{\nu_{AB}}=\frac{\pi e^2}{mc}f_{BA}N_A\frac{h}{kT}e^{\frac{(E_B-E_A)-h\nu}{kT}}\varphi, \tag{5.113}$$

where dimensionless factor φ equals

$$\varphi=\frac{kT}{hc|B_B-B_A|}\frac{1}{Z_{vA}Z_{rA}}e^{-\frac{hc}{kT}\left(\frac{1}{\lambda}-\frac{1}{\lambda_{00}}\right)}\times$$
$$\times\sum_{\text{bands}}\exp\left\{-\left[\omega_A v''+\frac{B_A}{B_B-B_A}\left(\frac{1}{\lambda}-\frac{1}{\lambda_{v''v'}}\right)\right]\right\}. \tag{5.114}$$

Here $\frac{1}{\lambda_{00}} = \frac{1}{hc}(E_B - E_A)$ as before is the wave number corresponding to electron transition in absence of vibrations and rotations (E_B and E_A are energies of electron states taking into account zero-point energy of vibrations $E = U_e + hc\omega/2$), $1/\lambda_{v''v'}$ is the wave number corresponding to transition Av" → Bv' in the absence of rotations. If $B_B > B_A$, bands have an edge with a "red" side and extend into "violet"; if, however, $B_B < B_A$, then it is the opposite (see formula (5.111)). Therefore, the sum over bands in (5.114) extends to bands with $\lambda_{v''v'} > \lambda$ when $B_B > B_A$ (as in the case of γ-system of NO) and to bands with $\lambda_{v''v'} < \lambda$ when $B_B < B_A$ (as in the case of β-system of NO or in Schumann — Runge system of O_2). This position is excellently illustrated by Figs. 5.24 and 5.25, on which are given in [21] values of sums in the factor φ depending upon wave length of light for γ- and β-systems of NO. Curves have a character of "paling," where every new tooth appears during inclusion in absorption of new band. In the case of γ-system absorption intermittently increases with decrease of λ, and in the case of β-system — with an increase of λ.

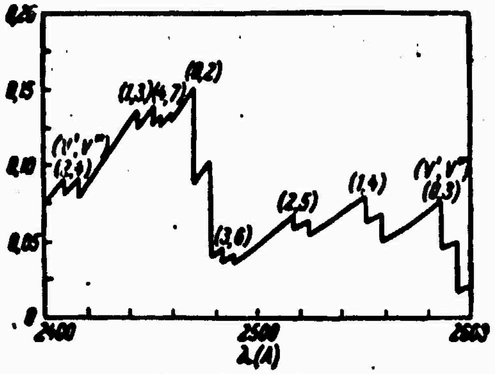

Fig. 5.24. Coefficient of spectral absorption in γ-system of NO in relative units. T = 8,000°K. Jump of absorption when λ = 2480 A corresponds to inclusion of vibrational transition 0-2.

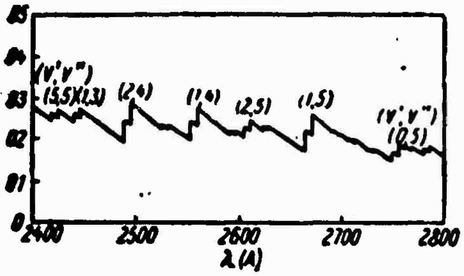

Fig. 5.25. Coefficient of spectral absorption in β-system of NO in relative units. T = 8,000°K.

A more exact formula (5.114) is turned into an approximate one (5.107), if one were sets factor φ, considering probability of different vibrational transitions, equal to one (inasmuch as formula (5.107) pertains to transition from ground state, then $E_A = 0$, $N_A = N$). Calculations show that coefficient φ not very strongly differs from 1, so that formula (5.107) can be used for a rough estimate.

We see that coefficients of molecular absorption can be theoretically calculated with the help of spectroscopic data about molecules, diagrams of levels, vibrational and rotational constants, potential curves, with an accuracy of constant factor — oscillator strength f, which should be determined from experiment. On figures 5.26-5.28 are given results of calculations of factors φ_λ at several temperatures for the most important systems of absorption,* determining absorbing properties of heated air: γ- and β-systems of NO, Schumann — Runge system of O_2, 1^+-, 2^+-systems of N_2 and 1^--system of N_2^+ (ionized molecule of nitrogen); values of $1/\lambda_{00}$ for these systems are presented in Table 5.6. A table of oscillator strength for these systems is presented in the following section. Figures 5.26-5.28 are taken from [8].

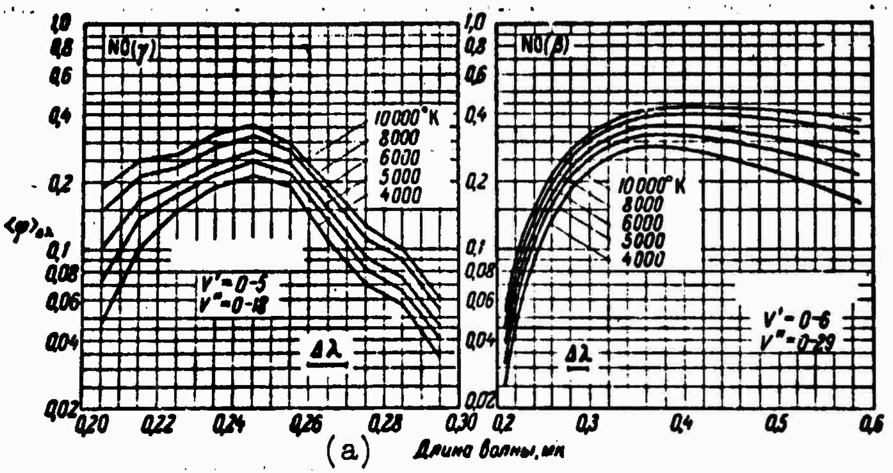

Fig. 5.26. Factor φ for γ- and β-systems of NO.
KEY: (a) length of wave μ.

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*φλ are smoothed by means of averaging in small intervals Δλ, which is necessary for comparison with experimental data, where Δλ is determined by equipment (monochromator).

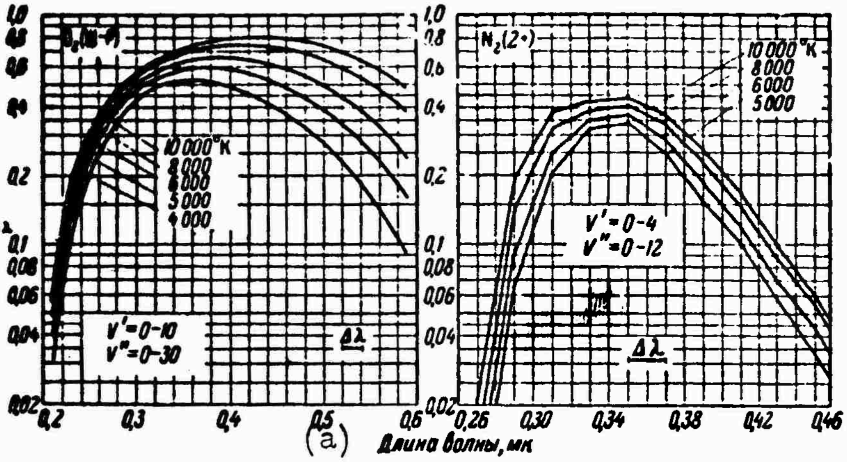

Fig. 5.27. Factor φ for Schumann — Runge system of O_2 and 2^+- system of N_2.
KEY: (a) length of wave, μ.

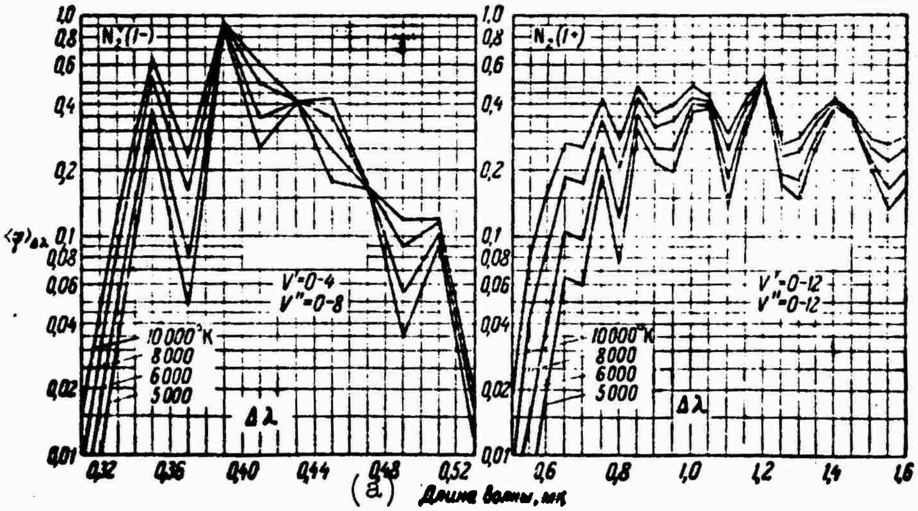

Fig. 5.28. Factor φ for 1^--system of N_2^+ and 1^+-system of N_2.
KEY: (a) length of wave, μ.

4. Air

§ 21. Optical Properties of Heated Air

The question about absorption and radiation of light by heated air has paramount value for such practically important problems, as study of phenomena occurring in the fireball of a strong explosion (see Ch. IX), calculation of radiation heating of ballistic rockets and artificial satellites upon entrance into atmosphere, and others. For the first problem a wide range of temperatures is essential from normal to hundreds of thousands and even a million degrees. For the second problem the most interest is in temperatures $\sim 5{,}000\text{-}20{,}000^{\circ}$K, which are developed in a shock wave before bodies moving in the atmosphere with speeds of the order of several or 10 km/sec. The range of densities with which it is necessary to deal is also wide, from $\sim 10\ \rho_0$ (in a shock wave propagated in air of normal density ρ_0) to very small $\sim 10^{-3}\text{-}10^{-4}\ \rho_0$ and even less, which is in central regions of fireball and at great heights.

Cold air, as is known, is transparent for visible light. Absorption starts in ultraviolet region of spectrum and is connected with system of Schumann — Runge bands of molecules of oxygen. Actually absorption attains noticeable magnitude when $\lambda \approx 1860$ A. An experimental curve of coefficient of absorption of cold air of normal density depending upon wave length is shown in Fig. 9.3 in § 2 IX.

At temperatures higher than $15{,}000\text{-}20{,}000^{\circ}$K, when molecules almost completely dissociate into atoms and the latter are noticeably ionized, absorption of light in continuous spectrum is composed of photoelectric absorption by atoms and ions and braking absorption in field of ions. These mechanisms were in detail considered in the first division of this champer, where estimation formulas were given for calculation of coefficients of absorption and mean free paths of radiation, based on approximation of hydrogen-likeness. In Table 5.2 § 8 were given results of calculations of mean free paths in air in the region of multiple ionization, i.e., at temperatures above approximately $50{,}000^{\circ}$K. At temperatures lower than $\sim 15{,}000^{\circ}$K in absorption all the above mechanisms participate while the comparative role of different components very strongly depends on frequency of light and on thermodynamic conditions: temperature and density. To components of continuous and quasi-continuous absorption belong: molecular transitions in molecules present in heated air N_2, O_2, N_2^+, NO, NO_2, photoelectric absorption by particles of O_2, N_2, NO, O, N, O^-, free-free transitions in field of O^+, N^+, NO^+, O_2^+, N_2^+, ions and also, possibly, in field of neutral atoms and molecules.

For specific calculations of coefficients of absorption, knowledge of concentrations of all shown components of air, and also concentration of free electrons (see Ch. III) is necessary, of course.

Optical properties of heated air were experimentally investigated with using a shock tube in an AVCO laboratory in the United States. Experimental and calculation data are presented in [8, 31, 32, 32a, 43-46] and surveys [28, 30, 47] (see also [33, 48]). The basic result of the experiments is determination of oscillator strengths for the most important molecular transitions.

By experiment is measured spectral intensity of radiation of a column of heated gas at different temperatures and densities. In a direct impact wave are studied temperatures of the order of 3,000-5,000°K, in a reflected wave — of the order of 8,000°K. Recalculation of measured intensities on coefficient of absorption can be made with help of the known formula for radiation flux from a heated layer of a given thickness d (see § 7, Ch. II, formula (2.38)). Namely, quantity of radiant energy in wavelength interval dλ, given off in 1 sec from a 1 cm^2 surface of a layer in unit of solid angle normal to the surface, equals

$$I_\lambda d\lambda = I_{\lambda p} d\lambda (1 - e^{-\varkappa'_\lambda d}), \qquad (5.115)$$

where $I_{\lambda p}$ is corresponding magnitude for an ideal black body

$$I_{\lambda p}=\frac{2hc^2}{\lambda^5}\frac{1}{e^{\frac{hc}{kT\lambda}}-1},$$

and $\varkappa'_\lambda = \varkappa_\lambda(1 - e^{-hc/kT\lambda})$ is the coefficient of absorption, corrected on forced emission. If the shell is optically thin, self-absorption in it can be disregarded (even in centers of lines): $\varkappa'_\lambda$ d << 1. Intensity of radiation in this case is determined by radiating ability:

$$I_\lambda=\frac{J_\lambda d}{4\pi}=I_{\lambda p}\varkappa'_\lambda d.$$

The ratio of measured intensity of radiation from calculation on shell of unit thickness to intensity of ideal black body gives directly corrected coefficient of absorption $\varkappa_\lambda$. Oscillator strength for system of Schumann — Runge bands was determined by means of investigation of intensity of radiation in pure oxygen at comparatively low temperatures ~3,000-4,000°K, obtained in a direct wave.

With such temperatures the degree of ionization is very small, absorption of negative ions of oxygen and practically all absorption is connected with molecular transitions. From these data on formulas (5.113), (5.114) with use of calculation coefficients $\varphi\lambda$ oscillator strength was deduced $f_{Sch-R} = 0.028 \pm 0.008$. In the wavelength interval from 3,300 to 4,700 A it turned out that it did not depend on λ, T, ρ.

Data on oscillator strengths of NO and N_2 were obtained by means of treatment of spectra of radiation in air at various temperatures and densities.

These magnitudes were extracted consecutively during the study of those sections of the spectrum, of temperatures and densities at which still unknown mechanisms play a small role, with the exception of one; absorption due to already known mechanisms was excluded from measured magnitudes.

Thus, were found oscillator strengths for all important systems;* they are gathered in Table 5.8.

Table 5.8. Oscillator Strength for the Most Important Systems of Bands

System	O_2(III–P)	NO_β	NO_γ	$N_2(2^+)$	$N_2^+(1^-)$	$N_2(1^+)$
f Error Interval λ, A	0,028 ±0,008 3300–4700	0,006 ±0,002 3500–5000	0,001 ±0,0005 2500–2700	0,09 ±0,03 2900–3300	0,18 ±0,07 3300–4500	0,025 ±0,008 10460

In Fig. 5.29 are depicted experimental and theoretically calculated intensities of radiation when T = 8,000°K $\rho = 0.83\rho_0$.

Formulas for calculation of coefficients of absorption of air:

$$\varkappa_{i\,\text{molec}} = \frac{10^{8} c_i \frac{Q}{Q_0}}{T^{\circ}} e^{\frac{h\nu}{kT}} \times \begin{cases} 9{,}5\varphi_{\text{III-P}}\, e^{-\frac{71\,000}{T}} & \text{system Schumann - Runge } O_2, \\ 2{,}04\varphi_\beta e^{\frac{65\,300}{T}} & \beta\text{-system } NO, \\ 0{,}34\varphi_\gamma e^{\frac{63\,500}{T}} & \gamma\text{-system } NO, \\ 30{,}6\varphi_{2+} e^{\frac{127\,500}{T}} & 2^+\text{-system } N_2, \\ 8{,}5\varphi_{1+} e^{\frac{84\,900}{T}} & 1^+\text{-system } N_2, \\ 61{,}2\varphi_{1-} e^{\frac{36\,800}{T}} & 1^-\text{-system } N_2^+, \end{cases}$$

$$\varkappa_{0^-} = 2{,}67\cdot 10^{19} c_{0^-} \frac{Q}{Q_0} \sigma_{0^-}$$

$$\varkappa_{i(\text{Kramers})} = \frac{2{,}56\cdot 10^{12} c_i \frac{Q}{Q_0}}{T^{1/2} x^3} e^{\frac{h\nu}{kT}} \times \begin{cases} e^{-\frac{140\,000}{T}} & O_2, \\ e^{-\frac{181\,000}{T}} & N_2, \\ e^{-\frac{158\,000}{T}} & O, \\ e^{-\frac{189\,000}{T}} & N, \\ e^{-\frac{108\,000}{T}} & NO \end{cases}$$

$$x = \frac{h\nu}{kT} = \frac{1{,}44}{\lambda T}$$

$$\varkappa_{NO_2} = 2{,}67\cdot 10^{19} c_{NO_2} \frac{Q}{Q_0} \sigma_{NO_2} \quad (T \text{ in } {}^\circ K,\ \lambda \text{ in cm},\ \varkappa \text{ in cm}^{-1}).$$

For convenience of calculation of coefficients of absorption of air we cite numerical formulas for calculation of separate components

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*For $N_2(1^+)$-system f strongly depends on λ due to sharp change of internuclear distance with change of λ.

in regions of molecular absorption and first ionization, i.e., when $T \lesssim 20{,}000^{\circ}K$.

Concentrations c_i of all particles are determined in these formulas as the ratio of numbers of particles to number of initial molecules in cold air. In formulas for coefficients of molecular absorption are placed oscillator strengths from Table 5.8. Effective charge in formulas for Kramers absorption is taken equal to 1.*

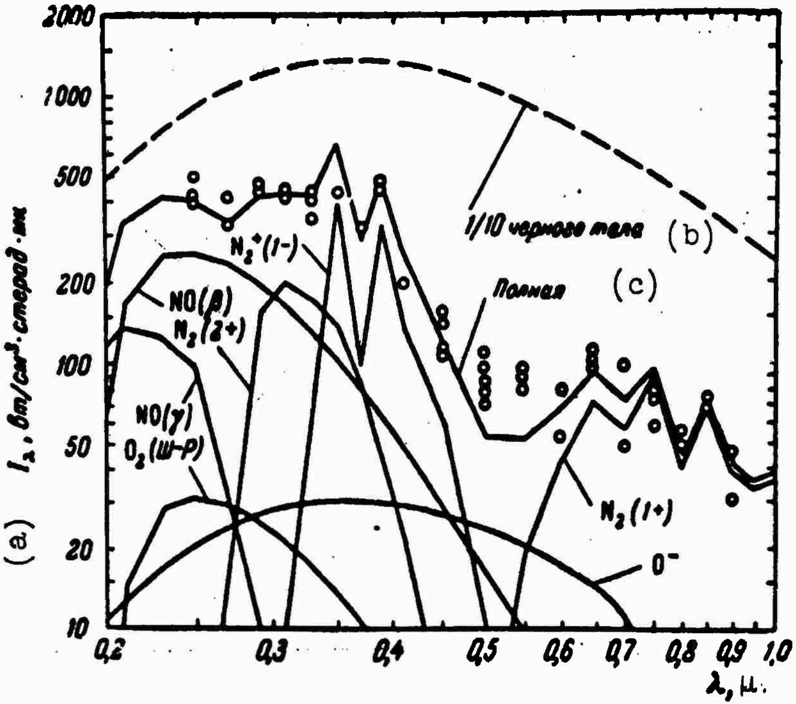

Fig. 5.29. Spectral intensity of radiation I_λ watt/cm^3·sterad·μ layer of air of thickness d = 1 cm. T = 8,000°K, ρ = 0, 83ρ_0 (ρ_0 — normal density). Shown are experimental points and calculated curves, corresponding to different mechanisms of emission. Dotted line gives magnitude 0.1 $I_{\lambda p}$ (1/10 intensity of radiation of black body). Ratio $I_\lambda/I_{\lambda p}$ gives directly $\varkappa'_\lambda$ cm^{-1}, inasmuch as d = 1 cm. The figure is taken from [8].

Concentration of negative ions of oxygen can be calculated by the

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*Correction factor of Bieberman and Norman (see § 7) is not considered.

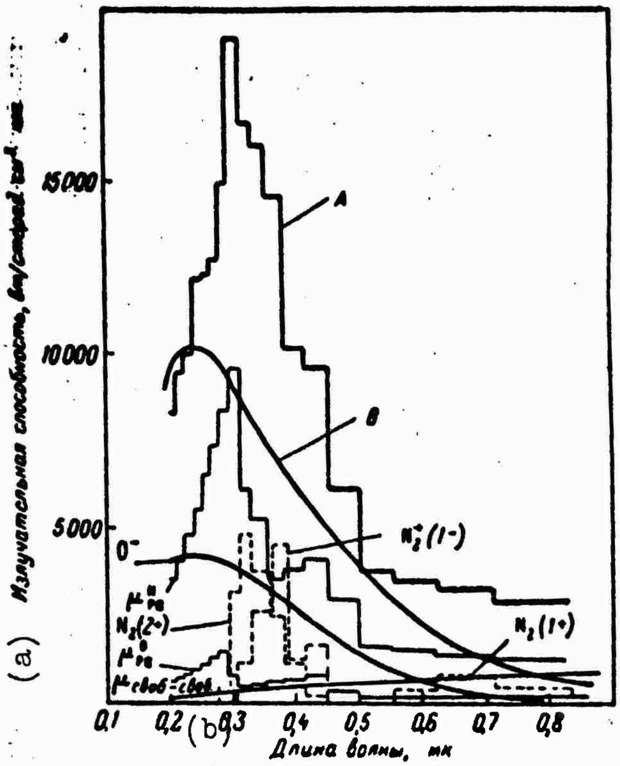

Fig. 5.30. Emission rate of air when $T = 12{,}000^\circ K$, $\rho = \rho_0$ (normal density). Shown are contributions of different mechanisms. μ_{P_e} — free-bound transitions; A — total radiation; B — 1/10 intensity of radiation of black body.

KEY: (a) emissivity, watt/sterad·cm^3·μ; (b) length of wave, μ.

formula of Saha, knowing the concentration of atoms of oxygen and free electrons. Effective absorption cross sections by negative O^- ions is given in Fig. 5.5 in § 5. Knowing all components of coefficients of absorption, it is possible to calculate total coefficients and radiative abilities for any temperatures and densities. On figures 5.30 and 5.31 is shown reconstruction of radiation obtained thus for several values of temperature and density (these data are borrowed from [28]). On graphs are shown contributions of individual components of absorption.

In [32] was investigated the question about free-free absorption

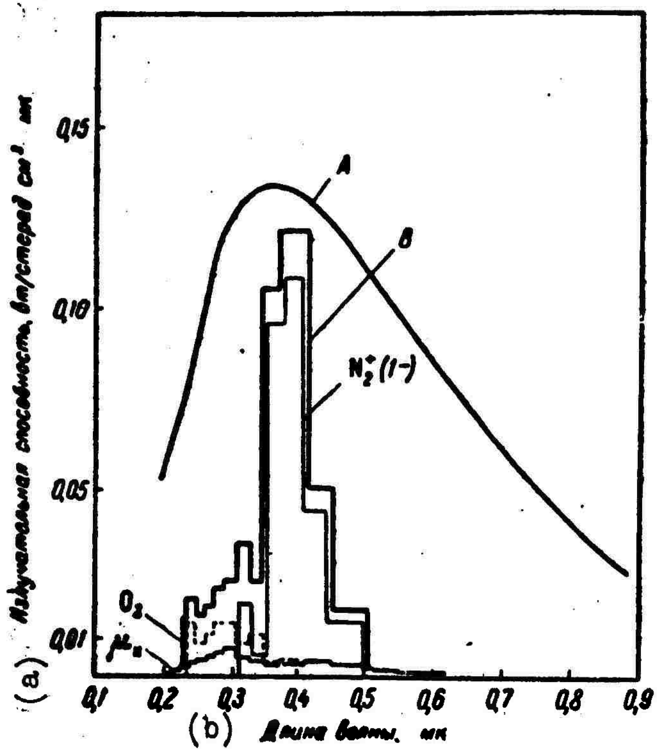

Fig. 5.31. Emission rate of air when $T = 8,000^\circ K$, $\rho = 10^{-3}\ \rho_0$. A - 10^{-5} intensity of radiation of black body, B — total radiation, μ_N — free-bound transitions.

KEY: (a) emissivity, watt/sterad$\cdot$cm$^3\cdot\mu$; (b) length of wave, μ.

by electrons in a field of neutral atoms. For this radiating ability was measured when $T = 8,000^\circ K$ $\rho/\rho_0 = 0.85$ in infrared region of spectrum with $\lambda \sim 20,000$-$40,000$ A, where by calculations all other mechanisms have to play a small role. It turned out that coefficient of absorption may be approximately described by the usual formula for brake absorption with square of effective charge $Z^2 = 0.04$ for O atoms and $Z^2 = 0.02$ for N. In visible and ultraviolet regions of spectrum, judging by these data, a free-free absorption in field of neutral atoms does not have to play a role.

Coefficients of absorption of red light $\lambda = 6500$ A in air in a shock wave for two values of temperatures were measured by I. Sh. Model'

[34]. In the experiments of I. Sh. Model' a detonational wave emerged from explosive on boundary with air. By photographic means change in time of luminous intensity of surface of front of shock wave in a direction normal to surface was measured. If d is thickness of layer of air enveloped by shock wave to moment t, then luminous intensity of surface of front is determined by formula (5.115). When shell of heated air becomes optically thick $\varkappa'_\nu d \gg 1$, the front gleams like a black body and $I_\nu \approx I_{\nu p}$. Taking curve of build-up of glow $I_\nu(d)$, it was possible to measure coefficient of absorption. Independently temperature was determined after the front according to brightness of front in the stage when $\varkappa'_\nu \gg 1$ and the front gleams like a black body. I. Sh. Model' obtained values of coefficient of absorption for two temperatures, $T = 10{,}900^\circ K$, $\varkappa_\lambda = 3.7\ cm^{-1}$; $T = 7480^\circ K$, $\varkappa_\lambda = 1.66\ cm^{-1}$ ($\lambda = 6{,}500$ A, $\rho/\rho_0 \approx 10$). The first value satisfactorily agrees with the value calculated by the given formulas.

A basic role is played by absorption in the 1^+-system of N_2 and by the Kramer mechanism. Regarding, however, the second point, the experimental value is much higher than that given in theory.*

A characteristic feature of all the above components of absorption (see summary of formulas pp. 438-440 is a sharp, Boltzmann dependence on temperature with very considerable energies of activation. At not very high temperatures of the order of $3{,}000$-$4{,}000^\circ K$ all coefficients in visible region of spectrum become very small; for instance, when $T = 4{,}000^\circ K$ and $\rho/\rho_0 = 1$ $\varkappa \sim 10^{-6}\ cm^{-1}$.

At such low temperatures a basic role in absorption is played by molecular absorption by nitrogen peroxide, which is present in air in insignificant quantities (see Table 5.9),** but strongly absorbs light

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*It is impossible to express defined judgement about causes of this divergence.

**Concentrations of NO_2 were calculated in [39].

in visible and ultraviolet regions of spectrum. Molecular bands of

Table 5.9. Equilibrium Concentrations of Nitrogen Peroxide in Heated Air, $c_{NO_2} \cdot 10^4$

ρ/ρ_0 / T, °K	10	5	1	ρ/ρ_0 / T, °K	10	5	1
2000	1,11	0,79	0,35	3500	2,91	1,92	0,79
2600	2,02	1,42	0,63	4000	2,86	1,90	0,67
3000	2,24	1,58	0,69	5000	2,11	1,29	0,25

Note: c_{NO_2} = number of molecules of NO_2/number of initial molecules in air.

NO_2 form a very complicated system with practically overlapping lines. In Fig. 5.32 is given dependence of effective absorption cross section of cold molecules of NO_2 according to [35]. The cross section monotonically drops from $\sigma = 6.5 \cdot 10^{-19}$ cm^2 to $\sigma \approx 10^{-20}$ cm^2 in wavelength interval from $\lambda = 4,000$ A to $\lambda = 7,000$ A. According to measurements of [36] absorption cross section in infrared region is very small: when $\lambda = 10,000$-$20,000$ A $\sigma < 4.5 \cdot 10^{-23}$ cm^2.

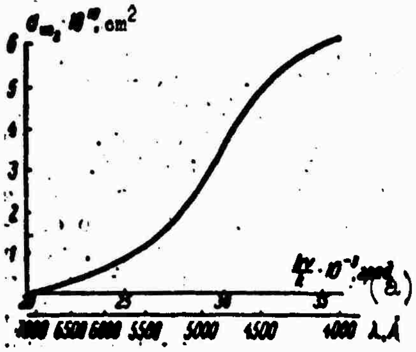

Fig. 5.32. Averaged effective absorption cross section of light by unexcited molecules of NO_2.
KEY: (a) degree.

In close ultraviolet region when $\lambda = 3020$ A the cross section passes through a minimum [37]; this together with curve of Fig. 5.32 indicates that maximum of absorption lies in blue part of spectrum $\lambda \sim 4,000$ A.

It is necessary to expect that at temperatures of the order of 2,000-4,000°K absorption spectrum is strongly displaced in red side and effective cross section of NO_2 in all visible region of spectrum becomes of the order of several units on 10^{-19} cm^2 (for greater detail see article [38]; see also

§ 7 Ch. IX).

For instance, during concentration of NO_2 molecules in air of the order of 10^{-4} this gives a coefficient of absorption at normal density of the order of 10^{-3} cm^{-1}.

In conclusion, once again we will stress that the question about optical properties of heated air is still very far from its final solution. In a number of cases there are deviations between theory and experiment and values of oscillator strengths for molecular transitions are impossible to consider fully reliable.

Literature

1. L. D. Landau and Ye. M. Lifshits. Field theory, Fizmatgiz, 1960.

2. L. D. Landau and Ye. M. Lifshits. Quantum mechanics, Part I, State Technical Press, 1948.

3. V. Gaitler. Quantum theory of radiation, IL, 1956.

4. D. Menzel and C. Pekeris. Monthly Notices 96, 77 (1935).

5. G. Bete and E. Solpiter. Quantum mechanics of atoms with one and two electrons, Fizmatgiz, 1960.

6. V. A. Ambartsumyan, E. R. Mustel', A. B. Severnyy, and V. V. Sobolev. Theoretical astrophysics, State Technical Press, 1952.

7. D. K. Bates. Collection of contemporary problems of astrophysics and solar physics, IL, 1950.

8. J. C. Keck, J. C. Camm, B. Kivel, and T. Wentink. Annals of Physics 7, 1 (1959).

9. L. M. Branscomb, B. S. Burch, S. J. Smith, and S. Geltman. Phys. Rev., 3, 504 (1958).

10. A. Unsöld. Physics of stellar atmospheres, IL, 1949. 2nd edition: A. Unsöld. Physik die Sternatmosphären, 1955.

11. A. Unsöld. Ann. Phys., 33, 607 (1938).

12. E. Vitensee. Z. Astrophys., 28, 91 (1951); H. Schirmer. Z. angew. Phys., 6, 3 (1954).

13. A. Burgess and M. J. Seaton. Rev. Mod. Phys., 30, 992 (1958); Mon. Not. Roy. Astron. Soc., 120, 121 (1960); 118, 504 (1958).

14. L. M. Biberman and G. E. Norman. Optics and spectroscopy, 8, 433 (1960).

15. L. M. Biberman, G. E. Norman, and K. N. N. Ul'yanov. Optics of spectroscopy, 10, 565 (1961).

16. S. Chandrasekhar and F. H. Breen. Astrophys. J. 103, 41 (1946); 104, 430 (1946).

17. L. M. Biberman and V. Ye. Romanov. Optics and spectroscopy, 3, 646 (1957).

18. Yu. P. Rayzer. ZhETF, 37, 1079 (1959).

19. R. Becker. Theory of electricity, 2, 2nd edition, Electron theory. State Technical Press, 1941.

20. a) G. Hertzberg. Spectra and structure of diatomic molecules, IL, 1949. See also:

b) A. G. Heidon. Energies of dissociation and spectra of diatomic molecules, IL, 1949.

c) V. N. Kondrat'yev. Structure of atoms and molecules, Fizmatgiz, 1959.

21. B. Kivel, H. Mayer, and H. Bethe, Annals of Physics 2, 57 (1957)

22. W. R. Jarmain, P. A. Fraser, and R. W. Nicholls. Astrophys. J. 118, 228 (1953); 119, 286 (1954); 122, 55 (1955); W. R. Jarmain and R. W. Nicholls. Canad. J. Phys., 32, 201 (1954); R. G. Turner and R. W. Nicholls. Canad. J. Phys., 32, 468 (1954); P. A. Fraser. Canad. J. Phys., 32, 515 (1954); R. W. Nicholls. Canad. J. Phys., 32, 722 (1954); R. W. Nicholls and W. Jarmain. Proc. Phys. Soc., A69, 253 (1956).

23. L. M. Biberman and I. T. Yakubov. Optics and spectroscopy, 8, 294 (1960).

24. S. A. Losev. Scientific Reports of the Higher Schools, Physical — mathematical sciences, No. 5, 197, 1958.

25. D. Weber and S. S. Penner. J. Chem. Phys., 26, 860 (1957).

26. R. Ditchburn and D. Heddle. Proc. Roy. Soc., A220, 61 (1953); A226, 509 (1954).

27. L. M. Biberman, S. P. Yerkovich, and V. N. Soshnikov. Optics and spectroscopy, 7, 562 (1959).

27a. V. N. Soshnikov. UFN, 74, 61 (1961).

28. R. E. Meyerott. Comb and Propuls. 3 ACARD. Colloc., 431, 1958. Translation: Problems of Rocket Technology, No. 11, 1959.

29. L. Landau and Ye. Lifshits. Statistical physics. State Technical Press, 1951.

30. J. Logan. Jet Propulsion 28, 795 (1958). Translation: Problems of Rocket Technology, No. 7, 18 (1959).

31. J. Keck, J. Camm, and B. Kivel. J. Chem. Phys., 28, 723 (1958).

32. T. Wentink, W. Planet, P. Hammerling, and B. Kivel. J. Appl. Phys., 29, 742 (1958).

32a. B. H. Armstrong and R. E. Meyerott. Phys. Fluids 3, 138 (1960).

33. S. A. Losev, N. A. Generalov, and L. B. Terebenin. Optics and spectroscopy, 8, 570 (1960).

34. I. Sh. Model'. ZhETF, 32, 714 (1957).

35. J. K. Dixon. J. Chem. Phys., 8, 157 (1940).

36. L. Harris and G. W. King. J. Chem. Phys., 2, 51 (1934).

37. C. R. Lambrey. C. R. Acad. Sci., 188, 251 (1922).

38. Yu. P. Rayzer. ZhETF, 34, 483 (1958).

39. Yu. P. Rayzer. Journal of Physical Chemistry, 33, 700 (1959).

40. S. Penner. Quantitative Molecular Spectroscopy and Gas Emissivities, London, 1959.

41. M. A. Yel'yashevich. Atomic and molecular spectroscopy, 1962.

42. A. P. Dronov, A. G. Sviridov, and N. N. Sobolev. Optics and spectroscopy, 12, 677, 1962.

43. B. Kivel, P. Hammerling, and J. D. Teare. Planet and Space Sci., 3, 132, 1961.

44. B. Kivel. J. Aero Space Sci., 28, 96, 1961.

45. R. A. Allen, J. C. Camm, and J. Keck. J. Quantit. Spectrosc. and Radiat. Transfer 1, No. 3-4, 269, 1961 (1962).

46. D. B. Olfe. J. Quantit. Spectrosc. and Radiat. Transfer 1, 3-4, 169, 1961 (1962).

47. S. S. Penner. Fundam. date obtained shock-tube experim. Oxf., Lond., N. Y., Paris Pergamon Press 221, 261, 1961.

48. F. S. Faynullov, N. N. Sobolev, and Ye. M. Kudryavtsev. DAN, 127, 541, 1959.

49. L. M. Biberman, V. S. Vorob'yev, and G. E. Norman. Optics and spectroscopy, 14, No. 3, 330 (1963).

CHAPTER VI

SPEED OF RELAXATION PROCESSES IN GASES

1. Molecular Gases

§ 1. Establishment of Thermodynamic Equilibrium

The state of a gas depends on concentrations of different components; atoms, molecules, ions, electrons, and distribution of internal energy with respect to degrees of freedom. In general the internal energy of a gas is composed of energy of translational motion of particles, rotational, and vibrational energy of molecules, chemical energy, ionizing energy, and electron excitation of atoms, moleucles, ions. In conditions of total thermodynamic equilibrium the state is completely determined by element composition of gas mixture and values of any two macroscopic parameters, for instance, density and specific internal energy.

Excitation of each of the degrees of freedom* and establishment of thermodynamic equilibrium require a certain time, the scale of which is the so-called relaxation time. Relaxation times for

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*For brevity we will talk about dissociation, chemical transformations, ionization as about "degrees of freedom."

excitation of different degrees of freedom are frequently very strongly distinguished; therefore, there are possible such conditions when thermodynamic equilibrium is established not in all, and only in part of the degrees of freedom. Most likely equilibrium is established in translational degrees of freedom of particles. If in the initial moment there existed some arbitrary distribution of atoms or molecules with respect to speeds, then after a few elastic collisions of particles with close masses, distribution with respect to speeds in these particles becomes Maxwellian. Establishment of Maxwellian distribution occurs as a result of an exchange of momentum and kinetic energy of particles, where during collisions of particles with masses not strongly distinguished momentum and energy are exchanged, which on the average are of such order as actual momentum and energy of colliding particles. Therefore, relaxation time for establishment of Maxwellian distribution in particles of a given sort or in particles of various sorts, but with close masses, has an order of the average time between gas kinetic collisions:

$$\tau_{\text{пост}} \sim \tau_{\text{газ}} = \frac{l}{\bar{v}} = \frac{1}{n\bar{v}\sigma_{\text{газ}}}, \tag{6.1}$$

where l is average gas kinetic range, $\overline{v}$ is average velocity of particles, n is number of particles in 1 cm^3, and σ_{gas} is gas kinetic effective cross section. For instance, in air under normal conditions $l \approx 6 \cdot 10^{-6}$ cm, $\tau_{trans} \sim 10^{-10}$ sec.

Usually gas kinetic times are very small as compared to times during which macroscopic parameters of gas, let us say, density and energy change in a noticeable way. Therefore, as a rule, it is possible in every moment to add to gas "translational" temperature — a magnitude characterizing average kinetic energy of translational motion of particles.* In a state of incomplete thermodynamic equilibrium, when one talks about thermodynamically equilibrium degrees of freedom, we consider that distribution of energy (and concentrations of corresponding components of gas mixture) in these degrees of freedom is in equilibrium with "translational" temperature of gas.

Magnitudes corresponding to unbalanced degrees of freedom, can be arbitrary; they depend on many factors, including the preceding "history" of the process in which gas participates.

Such conditions are met in rapidly occuring gas-dynamic processes or in regions of sharp change of macroscopic parameters, for instance, in ultrasonic wave or in front of shock wave, when time scales of the phenomenon** turn out to be comparable or even much smaller than corresponding relaxation times. In this case distributions of energy and concentrations of corresponding particles are determined not simply by temperature, density, and element composition of gas, as during thermodynamic equilibrium, but even by the kinetics of physico-chemical processes leading to establishment of equilibrium in given degrees of freedom.

In certain cases relaxation times for estabilshment of thermodynamic equilibrium in a specific degree of freedom are so large that

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*It is necessary to note that during isotropic distribution of particles with respect to directions of speeds of translational motion pressure of gas is determined by energy of translational motion of particles which are in 1 cm^3 E_k: $p = 2E_k/3$, absolutely independent of what the distribution of particles with respect to absolute values of speeds is, i.e., whether or not Maxwellian distribution and "temperature" exist.

**In a shock wave this is the time of sharp compression of gas.

the unbalanced state of the system turns out to be very stable, stationary. Usually such a position appears in a mixture of gases capable of chemical transformation, which actually does not occur due to great activation energy necessary for flow of reaction. A typical example is the fulminating mixture $2H_2 + O_2$, which in a state of strict thermodynamic equilibrium at low temperatures had to completely turn into water. We speak of such cases as "false" equilibriums.

As was already noted above, relaxation times for establishment of equilibrium in different degrees of freedom frequently very strongly are distinguished. If at a given temperature and density we pass from fast to slower relaxation processes, then usually it is possible to establish such a sequence: translational degrees of freedom, rotation of molecules, vibration of molecules, dissociation and chemical reactions, ionization and electron excitation.

Owing to a very sharp distinction in relaxation times, each of the relaxation processes may be studied individually, separating it from others and assuming that in easily excited degrees of freedom equilibrium exists in every moment, and slower relaxation processes do not take place during the period of the considered times.

All relaxation processes possess certain general patterns, independently of their nature. Namely, approach to state of thermodynamic equilibrium in given degree of freedom occurs asymptotically, according to the exponential law. If one were to characterize "state" of given degree of freedom by some parameter, let us say, number of particles N (for instance, number of molecules whose vibrations are excited, or number of molecules of a given sort in the case of chemical transformations), then at a given temperature and density (and element composition) the gas may be written

$$\frac{dN}{dt}=\frac{N_p-N}{\tau}, \qquad (6.2)$$

where N_p is the equilibrium number of particles, and τ is a certain magnitude of dimension of time, which characterizes speed of approach to equilibrium. From solution of equation (6.2)

$$N=N_{\text{нач}}e^{-\frac{t}{\tau}}+N_p\left(1-e^{-\frac{t}{\tau}}\right) \qquad (6.3)$$

it is clear that τ is relaxation time for given process. In general, the kinetics of physico-chemical processes by far are not always described by a linear equation of type (6.2). However, in stage of approach to equilibrium, when $|N_p - N| \ll N_p$, equation (6.2) is accurate as first approximation, if in the general equation of kinetics of the type

$$\frac{dN}{dt}=f(N, T, \rho, \ldots) \qquad (6.4)$$

we present the function in the right side in the form of an expansion with respect to a small deflection from equilibrium $(N_p - N)/N_p$.

It is necessary to say that time τ, determined by equation (6.2), as a rule, characterizes scale of times of establishment of equilibrium and in the case of the general equation of kinetics (6.4) (in this we will check by a series of specific examples in subsequent sections).

Consideration of kinetics of physico-chemical relaxation processes has two aspects. First, the question about speeds of elementary processes, leading to excitation of one or another degree of freedom, i.e., question about effective cross sections of corresponding nonelastic collisions of particles, as a result of which excitation occurs. Usually by these cross sections is also determined characteristic relaxation time τ. Secondly, the question about the actual kinetics of the relaxation process in given specific conditions taking into account the changing in time of macroscopic parameters of system and reverse influence of the process on change of macroscopic parameters. In this chapter we will stop only on the first of the shown aspects. (The second will be considered in Chapters VII, VIII). Here we will always assume that in gas are maintained constant temperature, density, and concentration of those particles which do not have a relation to the considered process.

§ 2. Excitation of Rotations of Molecules

Energies of rotation quanta of molecules are usually very small. Being divided by the Boltzmann constant, they have an order of several degrees, for instance, for oxygen it is 2.1°K, and for nitrogen it is 2.9°K. Therefore, even at room temperature $T \approx 300°K$, and even more so at high temperatures, quantum effects of rotations of molecules do not appear. Only the lightest molecules of hydrogen and deuterium are a certain exception, possessing very little moments of inertia and comparatively large rotation quanta – 85.4 and 43°K.

Due to "classicality" of rotations of a molecule during collisions translational and rotational energies are very intensely exchanged. Really, time of collision, i.e., time during which colliding molecules interact, is of the order a/v, where a is dimension of molecule, and v is average thermal speed. If energy of rotations is of the order of kT, then time of collision is comparable with period of rotation.* Consequently, the collision of molecules can be presented as the collision of two slowly turning "dumbbells" and sufficiently small asymmetry during approach of particles, so that they obtain a noticeable rotational moment.

Experimental data confirm the fact that rotations are easily excited. With the exception of H_2 and D_2, rotational energy of molecules attains its equilibrium classical value kT (for diatomic molecules) after ten gas kinetic collisions. Times of rotational relaxation were measured by experiment mainly by means of the study of dispersion and absorption of ultrasonics (for more about this method, see § 3, 4 Ch. VIII). They are in qualitative agreement with measurements of Corning and Green [1-3] of thickness of the front of weak shock waves according to reflection of light (for more about this method, see § 5 Ch. IV). Certain data about times of rotational relaxation and number of collisions necessary for establishment of thermodynamic equilibrium in rotational degrees of freedom of molecules are given in Table 6.1. More detailed data with numerous references to original works can be found in the surveys of L. V. Leskov and F. A. Savin [4] and S. A. Losev and A. I. Osipov [5].

With the exception of hydrogen at not too high temperatures, one may practically alawys assume that equilibrium in rotational degrees of freedom is established just as fast as in translational degrees, i.e., that rotations always have "translational" temperature.

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*Energy of rotations is of the order $kT \sim M\omega^2a^2$, where ω is angular frequency of rotations, M is mass of molecule. Period of rotations

$$t = \frac{2\pi}{\omega} \sim a\sqrt{\frac{M}{kT}} \sim \frac{a}{v}.$$

Table 6.1. Rotational Relaxation of Molecules

Molecules	Temperature, $^{\circ}K$	Relaxation time at atomsphere pressure, sec	Number of collisions	Method	Literature
H_2	300	$2.1\cdot10^{-8}$	300	Ultrasonics	[6]
H_2	300	$2.1\cdot10^{-8}$	300	Shock wave	[1]
D_2	288	$1.5\cdot10^{-8}$	160	Ultrasonics	[7]
N_2	300	$1.2\cdot10^{-9}$	9	Ultrasonics	[8]
N_2	300		20	Shock wave	[2,3]
O_2	314	$2.2\cdot10^{-9}$	12	Ultrasonics	[9]
O_2	300		20	Shock wave	[3]
NH_3	293	$8.1\cdot10^{-10}$	10	Ultrasonics	[10]
CO_2	305	$2.3\cdot10^{-9}$	16	Ultrasonics	[11]

§ 3. Equation of Kinetics for Relaxation of Vibrational Energy of Molecules

Energies of vibrational quanta of the most important diatomic molecules, being divided by the Boltzmann constant, have an order of a thousand or several thousand degrees; for instance, for oxygen $h\nu/k = 2230^{\circ}K$, for nitrogen it equals $3340^{\circ}K$. By formula (3.19) for vibrational energy of gas vibrational degrees of freedom give a noticeable contribution in heat capacity of gas, starting from temperatures at which kT is a few times less than $h\nu$. Thus, when $h\nu/kT = 4$ energy on one vibration composes 7.25% of its classical value kT, when $h\nu/kT = 3$-15%; for air of this temperature it is near $1000^{\circ}K$. Thus, in distinction from rotations of molecules the question about vibrational relaxation practically appears when vibrations have essentially a quantum character. Conversely, in the "far" classical region when $kT \gg h\nu$, let us say, at temperatures of the order of $10{,}000$-$20{,}000^{\circ}K$ the question loses, to a considerable degree, its timeliness, since in this case the molecules are basically dissociated into atoms. In the "far" classical region when $kT \gg h\nu$ for excitation of vibrations, as also for rotations of molecules, not many collisions are required. However, at those temperatures of the order of a thousand or several thousand degrees, when the question about vibrational relaxation presents practical interest, relaxation times are very great: for excitation of vibrations, as theory and experience show, thousands and hundreds of thousands of collisions are needed.

Let us formulate equation of kinetics for excitation of vibrations. Let us consider for simplicity gas from diatomic molecules of one sort. Let us assume that $T < h\nu/k$, so that excitation of only the first vibrational level of molecules* is essential (for air — this is temperatures of 1000-2000°K). If n_0, n_1, $n = n_0 + n_1$ is the number of unexcited, excited and all molecules in 1 cm^3, τ_{col} is the average time between gas kinetic collisions, determined by formula (6.1), and p_{10} and p_{10} [p_{01} ?] are the probabilities of excitation of vibrations and deactivation of excited molecule during collision, then the equation of kinetics can be written in the form

$$\frac{dn_1}{dt} = \frac{1}{\tau_{\text{ст}}}(p_{01}n_0 - p_{10}n_1). \qquad (6.5)$$

By principle of detailed balancing, in accordance with the law of Boltzmann,

$$\frac{p_{01}}{p_{10}} = \frac{n_{1p}}{n_{0p}} = e^{-\frac{h\nu}{kT}} \qquad (6.6)$$

(index p always notes equilibrium values).

Inasmuch as when $kT \ll h\nu$ $n_{1p} \ll n_{0p} \approx n$, we will obtain approximately:

$$\frac{dn_1}{dt} = \frac{n_{1p} - n_1}{\tau}, \qquad (6.7)$$

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*If the molecules are polyatomic, then we are limited to the case of excitation of only the most low-frequency vibrations.

where relaxation time

$$\tau = \frac{\tau_{\text{ст}}}{p_{10}} \tag{6.8}$$

is proportional to the number of collisions necessary for deactivation of molecule $-1/p_{10}$. Multiplying equation (6.7) by $h\nu$, we will obtain the equation for relaxation of vibrational energy of unit of volume $E = h\nu n_1 (E_p(T) = h\nu n_{1p}(T)$:

$$\frac{dE}{dt} = \frac{E_p(T) - E}{\tau}. \tag{6.9}$$

As we see, for excitation of vibrations equations of kinetics (6.7), (6.9) have the form of (6.2) during any deviations from equilibrium.

Let us consider now temperatures which are not small, $kT \gtrsim h\nu$, when in gas are present molecules which are in the most diverse vibrational states. In this general case one should write the system of equations of kinetics for numbers of molecules n_l, possessing l vibrational quanta ($l = 0, 1, 2 \ldots$). However, an equation of type (6.9) for relaxation of full vibrational energy all the same remains in force where relaxation time is determined by a formula which is only somewhat modified as compared to (6.8).

From quantum mechanics it is known* that if vibration is harmonic the oscillator can change its own energy only by a magnitude of one vibrational quantum, where probabilities of transition from a state with $l - 1$ quanta into a state with l quanta $p_{l-1,\, l}$ and transition from l-level to $l - 1$ level $p_{l,\, l-1}$ are proportional to l.

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*See, for instance the book by L. D. Landau and Ye. M. Lifshifts [2].

Thus, if we consider a molecule as a harmonic oscillator, which is accurate for not too high vibrational states, i.e., at temperatures which are not too large as compared to $h\nu/k$, then it is possible to write

$$p_{l-1,\,l} = lp_{01};\quad p_{l,\,l-1} = lp_{01};\quad l = 1, 2, 3, \ldots \tag{6.10}$$

The equation of kinetics for the number of molecules possessing l quanta taking into account transitions into the l-th state both from the $(l - 1)$-th, and also from the $(l + 1)$-th state, has the form

$$\frac{dn_l}{dt} = \frac{1}{\tau_{cT}}(p_{l-1,\,l}n_{l-1} + p_{l+1,\,l}n_{l+1} - p_{l,\,l-1}n_l - p_{l,\,l+1}n_l). \tag{6.11}$$

By the principle of detailed balancing, analogous to (6.6),

$$\frac{p_{l-1,\,l}}{p_{l,\,l-1}} = \frac{n_{l,\,p}}{n_{l-1,\,p}} = e^{-\frac{h\nu}{kT}}. \tag{6.12}$$

Let us multiply equation (6.11) by $h\nu l$. Putting (6.10) in (6.11), summarizing over l and noticing that $E = \Sigma h\nu l n_l$ is the total energy of vibrations in 1 cm^3, we will obtain

$$\frac{dE}{dt} = \frac{1}{\tau_{cT}}[p_{01}h\nu n - (p_{10} - p_{01})E], \tag{6.13}$$

where $n = \Sigma n_l$ is the total number of molecules in 1 cm^3. Considering (6.6) and the fact that magnitude $E_p = h\nu n(e^{h\nu/kT} - 1)^{-1}$ constitutes energy of vibrations in 1 cm^3 in conditions of thermodynamic equilibrium (see formula (3.19)), we will come to equation of kinetics

(6.9) with time of relaxation

$$\tau=\frac{\tau_{\text{ст}}}{p_{10}\left(1-e^{-\frac{h\nu}{kT}}\right)}. \qquad (6.14)$$

The average of collisions necessary for establishment of equilibrium in vibrational degrees of freedom equals

$$Z=\frac{1}{p_{10}\left(1-e^{-\frac{h\nu}{kT}}\right)}=\frac{Z_1}{1-e^{-\frac{h\nu}{kT}}}, \qquad (6.15)$$

where $Z_1 = 1/p_{10}$ is the number of collisions necessary for deactivation of a molecule possessing one vibrational quantum. When $h\nu \gg kT$ $Z = Z_1$ and formula (6.14) is turned into (6.8). At high temperatures, when the average of vibrational quanta in moleucles is great, $\bar{l} = kT/h\nu \gg 1$,

$$Z=\bar{l}Z_1, \quad \tau=\frac{\tau_{\text{ст}}\bar{l}}{p_{10}}=\frac{\tau_{\text{ст}}\bar{l}^2}{p_{\bar{l},\bar{l}-1}}.$$

In kinetic equation (6.11) for change of number of molecules in l-th quantum state only transitions accompanied by an exchange by energy between translational and vibrational degrees of freedom of molecules are taken into consideration. In fact during collisions of molecules also an exchange by vibrational quanta can occur, where it turns out that the probability of such an exchange is much larger than probability of exchange between translational and vibrational energies [13]. Therefore, Boltzmann distribution of molecules by vibrational levels in accordance with total reserve of vibrational energy of gas is established quickly. It is possible to say that in unbalanced system at first "vibrational" temperature is established, and then levelling of "vibrational" and "transitional" temperatures already occurs [14].

§ 4. Probability of Excitation of Vibrations and Relaxation Time

Let us consider the most simple case, when on diatomic molecule BC falls atom A along direction of axis of molecule, as was shown in Fig. 6.1. If between colliding particles A and BC there is no chemical affinity, then during the approach repulsive forces, appear between them, at first decelerating atom A, and then repelling it from molecule BC.

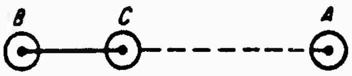

Fig. 6.1. Concerning the question of excitation of vibrations in molecule upon impact of atom.

On atom C acts coercive force, which at first tends to withdraw it from the position of equilibrium and to displace it in the direction of atom B. If approach occurs very slowly, atom C slowly will shift from the place and then, when atom A and molecule BC are repelled and start to move away from each other, also slowly return to the initial position: the blow, so to speak, will be "adiabatic" and vibration will not appear. The condition of adiabacity consists, obviously, in: so that time of interaction of atom with molecule, which has order a/v, where a is the range of operation of forces, and v is relative velocity of particles during infinite withdrawal, is great as compared to period of vibrations: $a\nu/v \gg 1$. Otherwise this condition can be imagined so: for "rocking" of molecule it is necessary that during decomposition of compelling force in Fourier integral there be great resonance components with frequencies close to natural frequency ν, but for this it is necessary that time of collision a/v be of the order $1/\nu$.

L. D. Landau and Ye. Teller [15] estimated the dependence of probability of excitation of vibrations on speed of collisions and, in the end, on temperature, using the conformity principle. For accuracy of quasi-classical approximation it is necessary that wave length of particles be small as compared to scale of field: $aMv/h \gg 1$, where M is reduced mass of colliding particles. It is easy to check that this condition is executed, if, along with the condition of adiabacity $a\nu/v \gg 1$, kinetic energy of relative motion is much larger than energy of quantum $Mv^2 \gg h\nu$.

The probability of excitation of vibration during collision is proportional to the square of the matrix element of energy of interaction of particles A and BC as a function of the distance between them U(x). In the quasi-classical approximation the matrix element is turned into a Fourier-component of energy of interaction:

$$\int_{-\infty}^{\infty} U[x(t)]\, e^{i2\pi\nu t}\, dt. \qquad (6.16)$$

Let us take the law of repulsion in the form $U = \text{const}\ e^{-x/a}$ and say for simplicity that const $= \mathcal{E} = Mv^2/2$, i.e., that an atom can "closely" approach a molecule. Integrating the equation of motion

$$\frac{dx}{dt} = \sqrt{\frac{2}{M}(\mathcal{E}-U)}, \quad t = \int \frac{dx}{\sqrt{\frac{2}{M}[\mathcal{E}-U(x)]}}.$$

we will find function t(x), x(t) and hence dependence U(t):

$$U(t) \sim \frac{e^{\pm\frac{vt}{a}}}{\left(e^{\pm\frac{vt}{a}}+1\right)^2}, \quad \begin{array}{ll} (+)\ \text{when} & -\infty < t < 0, \\ (-)\ \text{when} & 0 < t < \infty \end{array}$$

($t = 0$ corresponds to the biggest approach of particles).

To estimate integral (6.16) let us turn to integration with respect to a new path in complex plane t, passing along the straight line in the upper half-plane, parallel to real axis and distant from it at a distance of the pole of function $U(t)$ nearest to real axis: $t_1 = i\pi a/v$. It is easy to see that the integral is proportional to the exponential factor $\exp(-2\pi^2 a\nu/v)$, and probability of vibrational transition is proportional to $\exp(-4\pi^2 a\nu/v)$, i.e., exponentially drops with increase of factor of adiabacity $a\nu/v$. Probability, as a function of relative velocity of particles v, must be averaged with the help of Maxwellian distribution with respect to relative speeds, i.e., with the help of a function proportional to $\exp(-Mv^2/2kT)$. Here appears integral with respect to speeds contained in integrand exponential factor $\exp(-4\pi^2 a\nu/v - Mv^2/2kT)$. A basic role in the integral is played by speeds $v^* = (4\pi^2 a\nu kT/M)^{1/3}$ at which index of exponential has least absolute value. Collisions with such speeds are mainly caused by excitation and deactivation of vibrations. Integral and probability of transitions p_{01} and p_{10} are proportional to maximum value of exponential factor:*

$$p_{10} \sim p_{01} \sim \exp\left(-\frac{4\pi^2 a\nu}{v^*} - \frac{Mv^{*2}}{2kT}\right) = \exp\left(-\frac{3}{2}\frac{Mv^{*2}}{kT}\right) = \exp\left[-\left(\frac{54\pi^4 a^2\nu^2 M}{kT}\right)^{\frac{1}{3}}\right]. \qquad (6.17)$$

Substitution of numerical values of constants in index of

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*It is curious to note that likewise, according to the law $\exp(-\text{const}\ T^{-1/3})$, rate of thermonuclear reactions depends on temperature. This occurs because the probability of approach of nuclei repelled by Coulomb forces also depends on relative rate of approach according to the law $\exp(-\text{const}\cdot v^{-1})$, which is averaged with help of Maxwellian distribution with respect to speeds of nuclei.

exponential (6.17) and experiment show that at not too high temperatures the index much larger than unity.* This means that for collisions introducing basic a contribution into excitation and deactivation of vibrations, the condition of adiabacity holds and kinetic energy of colliding particles is much larger than kT.

Quantum-mechanical calculations of probability of deactivation p_{10}, determining relaxation time (Zener [17], Schwartz and Herzfeld [18]), also lead in adiabatic limit to a formula containing exponential factor (6.17). In [18] is considered the most general case of collisions and for a number of collisions before deactivation is obtained the formula:

$$Z_1 = \frac{1}{p_{10}} = \pi^2 \sqrt{\frac{3}{2\pi}} \left(\frac{h\nu}{\varepsilon_0}\right)^2 \left(\frac{kT}{\varepsilon_0}\right)^{\frac{1}{6}} e^{-\frac{h\nu}{2kT} - \frac{\varepsilon_1}{kT}} e^{\frac{3}{2}\left(\frac{\varepsilon_0}{kT}\right)^{1/3}}, \qquad (6.18)$$

where $\varepsilon_0 = 16\pi^4 a^2 \nu^2 M$. The last exponential factor accurately corresponds to exponential in (6.17) and at not too high temperatures owing to the great magnitude of the index describes basic temperature dependence of number of collisions. Factor exp $(-\varepsilon_1/kT)$ considers certain easing of transitions from acceleration of particles during their approach owing to long-range attractive forces, which are described by a "potential well" with energy ε_1; ε_1 is usually of the order of several tenth fractions of an electron volt. Formula (6.18) is somewhat definitized in a later work of Herzfeld, [18a].

As follows from the above-stated theory, time of vibrational

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*For instance, in oxygen when T = 1000°K the index equals approximately 10 (according to [16]; see below).

relaxation depends on temperature according to the law

$$\tau = Z\tau_{\text{CT}} = \tau_{\text{CT}} A \exp\left(bT^{-\frac{1}{3}}\right), \qquad (6.19)$$

where b = const, and A is a slowly changing function of temperature. Thus, graph ln τ depending upon $T^{-1/3}$ should give an almost straight line.

By experiment times of vibrational relaxation are measured at room temperature and small heating by the method of absorption and dispersion of ultrasonics, and in a wide range of temperatures with the help of shock tubes, by means of investigation of establishment of equilibrium in the front of a shock wave. A thorough investigation of relaxation in oxygen and nitrogen was conducted with the help of a shock tube by Blackman [16]. Its results are presented in Table 6.2. In the same place are given theoretical values for oxygen,

Table 6.2. Vibrational Relaxation in Oxygen and Nitrogen According to Measurements of Blackman [16]. Theoretical Values of Schwartz and Herzfeld [18].

T, °K	p_{10} (experiment)*	p_{10} (theory)	Number of collisions Z (experiment)	τ in sec reduced to density $n = 2{,}67 \cdot 10^{19}\ \frac{1}{\text{см}^3}$
	Oxygen			
288	$4 \cdot 10^{-8}$ **)	$1 \cdot 10^{-8}$	$2{,}5 \cdot 10^{7}$	
900	$1.1 \cdot 10^{-5}$	$3 \cdot 10^{-6}$	$1 \cdot 10^{5}$	$96 \cdot 10^{-7}$
1200	$2.4 \cdot 10^{-5}$	$1.3 \cdot 10^{-5}$	$5 \cdot 10^{4}$	$41 \cdot 10^{-7}$
1800	$9.8 \cdot 10^{-5}$	$8.6 \cdot 10^{-5}$	$1.4 \cdot 10^{4}$	$9.5 \cdot 10^{-7}$
2400	$3.7 \cdot 10^{-4}$	$5.5 \cdot 10^{-4}$	$4{,}5 \cdot 10^{3}$	$2.7 \cdot 10^{-7}$
3000	$1.2 \cdot 10^{-3}$	$1.5 \cdot 10^{-3}$	$1.6 \cdot 10^{3}$	$0.83 \cdot 10^{-7}$
	Nitrogen			
600	$3 \cdot 10^{-8}$	$3{,}3 \cdot 10^{7}$ ***)		
3000	$3.1 \cdot 10^{-5}$	$4.6 \cdot 10^{4}$		$2.1 \cdot 10^{-6}$
4000	$9.7 \cdot 10^{-5}$	$1.8 \cdot 10^{4}$		$0.67 \cdot 10^{-6}$
5000	$2.5 \cdot 10^{-4}$	$0.8 \cdot 10^{4}$		$0.27 \cdot 10^{-6}$

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*During calculation of p_{10} from experimental times τ are used gas kinetic sections σ_{O_2} = $3.6 \cdot 10^{-15}$ cm², σ_{N_2} = $4.1 \cdot 10^{-15}$ cm².

**This point is obtained by the ultrasonic method [1-].

***This point is obtained Kantrowitz [20] by means of investigation of outflow from nozzle.

calculated in the work of Schwartz and Herzfeld [18]. As can be seen, agreement between theory and experiment is not bad.

Experimental values measured for the most diverse gases more or less satisfactorily lie on theoretical straight lines ln τ or ln Z from $T^{-1/3}$. This may be seen from Fig. 6.2, borrowed from [5]. Deviations from straight lines partially are explained by temperature dependence of pre-exponential factor A in formula (6.19).

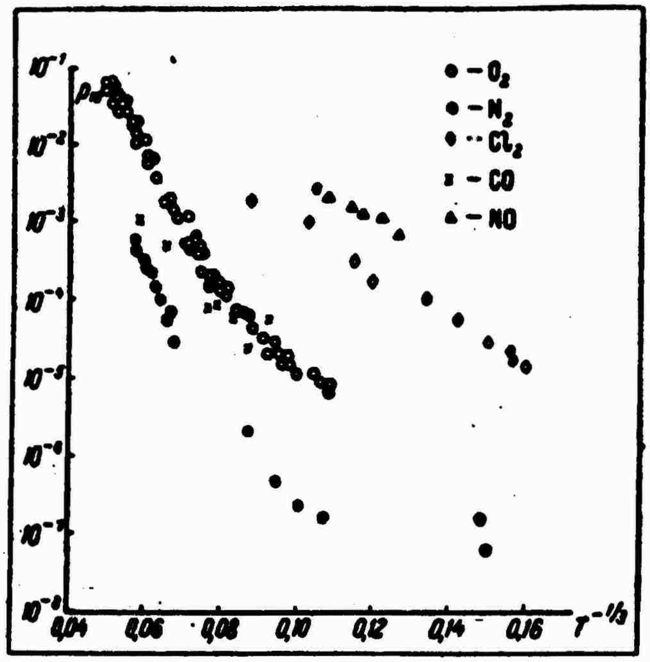

Fig. 6.2. Experimental data on probabilities of deactivation of molecules in which vibrations are excited.

Time of vibrational relaxation in oxygen with that same temperature is less than in nitrogen, since the natural frequency in nitrogen is one and a half times more than in oxygen which hampers excitation of vibrations in nitrogen. Therefore, vibrational relaxation in air has two periods: at first oxygen arrives in equilibrium, and then nitrogen. It is necessary to note that collisions of N_2

molecules with O_2 is 2.5 times less effective with respect to excitation of vibrations in O_2, than $O_2 - O_2$ collisions. In general, certain molecules very actively excite vibration; for instance, molecule of H_2O 50-100 times more rapidly excite vibrations in O_2, than the actual O_2 molecules. Therefore, during measurements of vibrational relaxation a high degree of gas scrubbing from impurities is essential.

Detailed summaries of source material on times of vibrational relaxation in different gases, just as references to numerous experimental and theoretical works, can be found in the surveys of L. V. Leskov and F. A. Savin [4] and S. A. Losev and A. I. Osipov [5]. Let us indicate several of the recent works on the study of excitation of vibrations in O_2 [58, 59], NO [60], CO [61], CO_2 [62, 63]. Let us note also a survey of [64] and work [65, 66] on vibrational relaxation in mixtures.

§ 5. Equation of Kinetics of Dissociation of Diatomic Molecules and Relaxation Time

Dissociation of diatomic molecules occurs usually during collisions of sufficiently energetic particles according to the scheme:

$$A_2 + M \rightleftarrows A + A + M, \qquad (6.20)$$

where M is any particle.* In uniform diatomic gas particle M can

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*Direct disintegration of a sufficiently strongly excited molecule into atoms $A_2 \rightleftarrows A + A$ has an extraordinarily small probability, just as the reverse process of unification of atoms into a molecule without participation of a third particle to which could be transmitted part of the energy given off during unification. There are also small probabilities of photodissociation and recombination with emission of light quantum.

be either molecule A_2, or atom A. The reverse process leads to recombination of atoms in three-body collisions, where third particle M takes on part of the binding energy given off.

The equation of kinetics for process (6.20) taking into account the fact that particle M can be both a molecule, and also an atom, has the form

$$\frac{dA_2}{dt} = -\frac{1}{2}\frac{dA}{dt} = -k_d A_2^2 + k_r A^2 \cdot A_2 - k'_d A_2 \cdot A + k'_r A^3. \qquad (6.21)$$

Here for brevity the numbers of particles in 1 cm^3 are designated by their symbols. Constants of rates of reactions depend only on temperature and are connected by the principle of detailed balancing:

$$\frac{k_d}{k_r} = \frac{k'_d}{k'_r} = \frac{(A)^2}{(A_2)} = K(T), \qquad (6.22)$$

where in parentheses are enclosed equilibrium values of numbers of particles for given temperature and density of gas; K(T) is the equilibrium constant, distinguished from equilibrium constant for pressures $K_p(T)$ by the factor $(kT)^{-1}$: $K(T) = K_p(T)/kT$. The equilibrium constant determines equilibrium degree of dissociation α at given temperature and density. By formula (3.26)

$$\frac{\alpha^2}{1-\alpha} = \frac{K(T)}{4N} = \frac{1}{4N}\frac{M_A \nu}{4I_{A_2}}\sqrt{\frac{M_A}{\pi kT}}\frac{g_A^2}{g_{A_2}}e^{-\frac{U}{kT}}, \qquad (6.23)$$

where N is the number of initial molecules in 1 cm^3, M_A is the atomic mass (for remaining designations see in § 3 Ch. III).

In distinction from vibrational relaxation, the equation of kinetics for dissociation of molecules in general is nonlinear. However, with a small deflection of it from equilibrium, it is possible in accordance with general indication in § 1 to bring to a linearized form (6.2) for numbers of particles A or A_2, where relaxation time τ is determined by expression

$$\frac{1}{\tau}=4\alpha(2-\alpha)N^2\left(k_r+k'_r\frac{2\alpha}{1-\alpha}\right). \qquad (6.24)$$

As calculations show, by time τ is characterized not only the final stage of asymptotic approximation to equilibrium, but also in general, all kinetics of dissociation, even in that stage when it is described by nonlinear equation (6.21), so that τ in order of magnitude is equal to time of establishment of equilibrium dissociation and in general of arbitrary initial conditions. In limiting cases of small and strong equilibrium dissociation formula (6.24) is simplified. When $\alpha \ll 1$ there are few atoms, a basic role is played by dissociation of molecules by impacts of molecules also taking into account (6.22), (6.23)

$$\frac{1}{\tau}=8\alpha N^2k_r=\frac{2}{\alpha}Nk_d. \qquad (6.25)$$

When $1-\alpha \ll 1$, if even in initial moment there are no atoms, the late stage occupies the main time, when there are few molecules and remaining molecules are smashed by the impacts of the atoms. In this case

$$\frac{1}{\tau}=\frac{8}{1-\alpha}N^2k'_r=2Nk'_d. \qquad (6.26)$$

Thus, the question about time of establishment of equilibrium leads to the question of rates of reactions of dissociation or recombination. Inasmuch as both rates are connected by the principle of detailed balancing (6.22), it is sufficient to know one of them from theory or experiment.

§ 6. Recombination Rates of Atoms and Dissociation of Diatomic Molecules

A rough estimate of the recombination rate of atoms in a diatomic molecule can be obtained from the most elementary considerations, assuming that every gas kinetic collision of atoms in the presence of a third particle leads to recombination. The number of collisions of A atoms with each other in 1 cm^3 in 1 sec equals $A \cdot \overline{v} \cdot \sigma \cdot A$, where $\overline{v} = (8kT/M_A\pi)^{1/2}$ is average thermal speed, and σ is gas kinetic cross section. The probability that at the time of collision "in the neighborhoods" i.e., at a distance of the order of molecular dimensions r, a third particle will appear, approximately is equal to average of particles in a volume equal to the volume of one molecule: $(4\pi r^3/3)N$, where N is the number of particles in 1 cm^3. Thus, the number of triple collisions in 1 cm^3 in 1 sec equals $A \cdot v \cdot \sigma \cdot A(4\pi r^3/3)N$. Introducing for generality the numerical coefficient β, equal to probability of recombination under the condition that a triple collision happened we will obtain for constant of recombination rate the expression:

$$k_r = \beta \overline{v} \sigma \frac{4\pi r^3}{3}. \qquad (6.27)$$

For instance, for atoms of nitrogen $\overline{v} = 3.9 \cdot 10^3 \sqrt{T^\circ}$ cm/sec,

$\sigma \approx 10^{-15}$ cm^2. Considering $r = 3.4 \cdot 10^{-8}$ cm and $\beta = 1$, we will obtain $k_r = 2.2 \cdot 10^{14} \sqrt{T^\circ}$ cm^6/mole^2·sec (in one mole there are $6 \cdot 10^{23}$ atoms). When T = 300°K $k_r = 3.8 \cdot 10^{15}$ cm^6/mole^2·sec.

Recombination of atoms of nitrogen is usually studied experimentally by measuring the change in time of the number of molecules of nitrogen according to the afterglow.* Thus was found constant of recombination rate with molecules of nitrogen as the third particle. In the interval of temperatures from 297° to 442°K it turned out to almost not depend on temperature and equal $k_r = 5.8 \cdot 10^{15}$ cm^6/mole^2·sec [21], in good agreement with the given estimate. Close results have been obtained by other authors [22, 23]).

In [70] by means of measurement of unbalanced radiation was studied dissociation and recombination of nitrogen in a shock tube. It was found that when T = 6400°K the constant of recombination rate equals $k_{rN} = 6.5 \cdot 10^{15}$ cm^6/mole^2·sec, if an atom of nitrogen serves as the third particle, and is 13 times less, if the role of third particle is played by a molecule of nitrogen.

In general, at not too high temperatures (T ~ 300-1000°K) constants of recombination rate usually have the order 10^{14}-10^{16} cm^6/mole^2·sec which points to rather large probabilities of recombination β during a three-body collision. The recombination rate comparatively weakly depends on temperature, usually manifesting a

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*The phenomenon of afterglow of nitrogen consists of the following: during recombination of atoms of nitrogen N_2 molecules turn out to be in an excited state $^5\Sigma_g^+$. Subsequent collisions with other molecules or atoms partially deactivate the molecules so that they pass into a lower state $B^3\Pi_g$, after which are emitted quantum of the first positive system $N_2(B^3\Pi_g \to A^3\Sigma_u^+)$, which are recorded by experiment. One judges kinetics of recombination according to change of luminous intensity.

certain tendency to decrease with temperature increase. This is possible to grasp, if one considers that the probability of recombination during a triple collision is even greater the larger the time of interaction of colliding particles, i.e., the less their speed or the less the temperature, so that probability β inversely depends on temperature. For instance, if $\beta \sim 1/T$, then $k_r \sim \overline{v}\beta \sim 1/T^{1/2}$ in accordance with theoretical calculations of Wigner [24].

The recombination rate of atoms depends on the kind of third particle; for instance, during recombination of atoms of nitrogen, atoms of nitrogen as third particles are 13 times more effective than molecules (when $T = 6400^\circ K$). In [25] the study of kinetics of dissociation of iodine in a shock tube (concentration of I_2 molecules was measured by absorption of light) showed that when $T = 1300^\circ K$ molecules of iodine are 35 times more effective as third particles during recombination of atoms of iodine than atoms of argon. Recombination rate of iodine in a three-body collisions with argon when $T = 1300^\circ K$ $k_r = 4.5 \cdot 10^{14}$ cm^6/mole$^2 \cdot$sec [25]; when $T = 298^\circ K$ $k_r = 2.9 \cdot 10^{15}$ cm^6/mole$^2 \cdot$sec [26].

Dissociation of a molecule upon collision with another particle can occur only in the case when energy of colliding particles exceeds energy of dissociation. The total number of collisions in 1 sec of a given molecule with other particles whose number in 1 cm^3 equals N, is $\nu = N\overline{v}'\sigma$, where $\overline{v}'$ is the average speed of relative motion of particles $\overline{v}' = (8kT/\pi\mu)^{1/2}$; μ is the reduced mass.* During

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*In estimating the recombination rate, for simplicity $\overline{v}'$ was replaced by $\overline{v}$, i.e., μ-atomic masses M_A.

a Maxwellian distribution with respect to speeds the number of collisions of molecules with kinetic energy of relative motion exceeding energy of dissociation U, composes the fraction $(U/kT + 1)e^{-U/kT}$ of the total number of collisions (usually $U/kT \gg 1$, so that $(U/kT) + 1 \approx U/kT$). It is considered that with respect to dissociation only that component of kinetic energy of particles which corresponds to component of relative speed directed along line of centers of colliding particles is effective (if the latter are considered as hard balls). In this assumption the fraction of "sufficiently energetic" collisions instead of $(U/kT) \exp(-U/kT)$ equals simply $\exp(-U/kt)$.

It is natural to think that on breaking the bond in a molecule not only kinetic energy of translational motion of colliding particles can be expended, but also energy of their internal degrees of freedom: vibrational, rotational. It is possible to show (see [27]) that the fraction of collisions in which total energy of colliding particles taking into account energy of internal degrees of freedom exceeds energy of dissociation, equals*

$$\frac{1}{s!}\left(\frac{U}{kT}\right)^{s} e^{-\frac{U}{kT}}.$$

where every vibrational degree of freedom introduces unity into index s, and every rotational degree of freedom introduces 1/2 (in the case of half-integral s factorial s! is replaced by gamma-function: $\Gamma(s + 1)$.

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*In deriving this formula it is considered that distribution of molecules by energy states in all internal degrees of freedom is Boltzmann, corresponding to translational temperature T.

At present the theory of dissociation of molecules by impacts of particles is very far from completion, therefore, during comparison with experiment for constant of speed of dissociation a formula of the shown type is usually used:

$$k_d = P\bar{v}'\sigma \frac{1}{s!}\left(\frac{U}{kT}\right)^s e^{-\frac{U}{kT}}. \qquad (6.28)$$

The number s, characterizing degree of participation in dissociation of internal degrees of freedom, and factor P, which constitutes probability that dissociation indeed will occur during collision of particles with sufficient reserve of energy for dissociation, are considered as parameters which one should determine from experiment.

According to contemporary ideas a basic role in dissociation is played by the vibrational energy of the moleucle. Ye. V. Stupochenko and A. I. Osipov [28] showed that the probability of dissociation of an unexcited molecule is extraordinarily small, even if translational energy of colliding particles exceeds binding energy U. Mainly molecules dissociate which are on very high vibrational levels whose energy is close to the energy of dissociation. Here energy of translational motion of particles can not strongly differ from average thermal energy.

If one were to assume that distribution of molecules by vibrational states is Boltzmann, then for rate of dissociation a formula of the type (6.28) remains in force with corresponding value of index s.

Ye. V. Stupochenko and A. I. Osipov [29] showed that this assumption is not always justified. The "drain" of molecules from highest vibrational levels due to dissociation can sometimes strongly disturb Boltzmann distribution of molecules by highest vibrational states. In this case kinetics of dissociation should be considered jointly with kinetics of excitation of highest vibrational states. The process occurs in such a way that owing to collisions molecules "are given" to upper levels, whence pass into a dissociated state. During recombination of atoms in the presence of a third particle energy of dissociation is transformed mainly into vibrational energy of the formed molecule. The theory of these processes is presented in survey [76].

By experiment was studied basically dissociation of oxygen after the front of a shock wave in a shock tube (work of Matthews [30], Byron [31], N. A. Generalov and S. A. Losev [32], Camac [67], Rink, and others [68]; for a survey of source material and references to other works, see in [4, 5]).

A thorough investigation was conducted by Matthews. By the interferometric method was determined movement of density in an unbalanced zone after a shock wave, which was compared with theoretical calculations carried out on the basis of the formula for rate of dissociation of type (6.28) (see Ch. IV: VII). Equilibrium in the vibrational degree of freedom is established at least an order faster than dissociation occurs,* so that effect of relaxation of vibrations does not hinder study of rate of dissociation. The 2000-4000°K region of temperatures was studied. The degree of dissociation in experiments of Matthews was small, $\alpha \sim 0.05-0.1$, so that the basic

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*Not too high vibrational states are considered, in which there is an overwhelming majority of molecules.

role in dissociation was played by $O_2 - O_2$ collisions.* In calculations it was assumed that S = 3; effectiveness of collisions turned out to equal $P_{O_2-O_2} = 0.073$, and constant of speed of dissociation:

$$k_{dO_2-O_2} = 5.4\cdot10^{19}T^{\circ\frac{1}{2}}\left(\frac{59\,380}{T^\circ}\right)^3 e^{-\frac{59\,380}{T^\circ}}\ \text{см}^3/\text{mole}\cdot\text{sec} \qquad (6.29)$$

Calculations conducted with s = 0 gave an improbably large value of P (larger than unity). This indicates that in dissociation an essential role is played by energy of internal degrees of freedom of molecules. Knowing equilibrium constant for dissociation O_2:

$$K(T) = 1{,}85\cdot10^{3}T^{\circ-\frac{1}{2}}e^{-\frac{59\,380}{T^\circ}}\ \text{mole/cm}^3 \qquad (6.30)$$

recombination rate with O_2 molecules as the third particles can be found:

$$k_r = 6.1\cdot10^{21}T^{\circ-2}\ \text{см}^6/\text{mole}^2\ \text{sec}^{**}. \qquad (6.31)$$

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*With the reaction $O_2 + O_2 = 2O + O_2$ competes a two-stage reaction of O_2 dissociation with intermediate formation of ozone $O_2 + O_2 = O + O_3$; $O_3 + M = O + O_2 + M$ (correspondingly the reverse process of recombination can also occur). At high temperatures this process plays a small role (in particular, in experiments of Matthews). However, recombination of oxygen at low temperatures and small degree of dissociation occurs mainly through formation of ozone, since $O + O + M$ collisions occur much rarer than $O + O_2 + M \rightarrow O_3 + M$ collisions. For constants of rates of reactions with participation of ozone, see in [33].

**This formula is accurate only in the investigated interval of temperatures $T \approx 2000$-4000°K. Extrapolation of it to room temperatures gives an oversized value of the recombination rate.

Relaxation time for $T = 3500^\circ K$ and normal density $\tau = 0.95 \cdot 10^{-6}$ sec ($\alpha = 0.084$). This result is very close to data of Glick and Wurster [34], measuring relaxation time for dissociation of oxygen in a shock tube. Their times, corrected to normal density, equal

T, °K	3100	3300	3400	3850
$\tau \cdot 10^6$ sec	2	0.8	0.5	0.06

In [35, 36, 25] was studied rate of dissociation of bromine and iodine (also in shock tube; concentration of molecules Br_2, I_2 was measured according to absorption of light from an outside source). In [35] in an interval of temperatures up to 2000°K for speed of dissociation of molecules of bromine by impacts of atoms of argon, is obtained: $s = 2$, $P_{Br_2-Ar} = 0.12$. Satisfactory agreement with this result is obtained in the theoretical work of Ye. Ye. Nikitin [37]. For a survey of works on dissociation of molecules, see in [5]. Let us note recent work [69], in which was studied dissociation of hydrogen in a shock tube. For rates of O_2 and N_2 dissociation and other relaxation processes in air see also [53].

§ 7. Chemical Reactions and the Method of the Activated Complex

From the point of view of energy effect chemical transformations are subdivided into two types: endothermic, requiring specific energy content, and exothermic, accompanied by liberation of heat. Examples of reactions of both types are dissociation of molecules and recombination of atoms into a molecule, considered above. It is clear that for an endothermic reaction it is necessary that colliding molecules possess certain minimum reserve of energy, so-called activation energy E, therefore, the rate of such a reaction is proportional to Boltzmann factor $e^{-E/kT}$ and increases rapidly with increase of temperature. In dissociation binding energy of molecule U serves as activation energy. Experiment, however, shows that for the majority of exothermic transformations energy of activation is also required and rates of corresponding reactions increase with temperature according to the exponential law $e^{-E/kT}$, called the law of Arrhenius. Recombination of atoms into a molecule is in this ratio untypical, since it occurs without activation and therefore easily occurs at low temperatures, as do many other reactions with participation of free atoms.

So that the elementary event of chemical transformation occurs, let us say, exchange by atoms during collision of molecule XY with molecule WZ:

$$XY + WZ \rightarrow XW + YZ \qquad (6.32)$$

is necessary in order that there be a close approach of molecules of reagents. Independently of whether this process is energetically profitable or not, i.e., energy is given off or absorbed as a result of exchange, during close approach of particles between them, as a rule, appear repelling forces, to surmount which is necessary a specific energy. It is possible to say that for transformation a potential barrier should be surmounted. This position is explained in Fig. 6.3, on which is plotted the potential energy of a system of four atoms XYWZ depending upon "coordinate of decomposition," characterizing mutual space configuration of atoms. For definity it is assumed that forward process (6.32) is exothermic. The difference

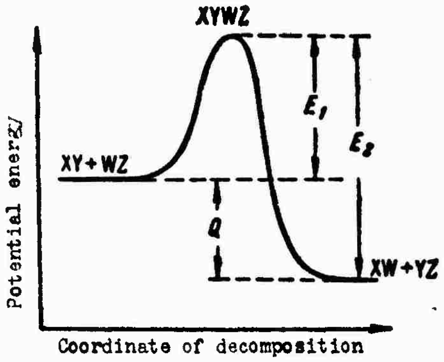

Fig. 6.3. Concerning the question of potential barrier during chemical reactions.

of energies between initial and final states of the system is equal to energy reaction yield Q. From Fig. 6.3 it is clear that activation energy of reverse process E_2 exceeds activation energy of forward process E_1 by the magnitude of energy of reaction Q. Correspondingly the rate of the reverse, endothermic, reaction much more sharply depends on temperature than does rate of forward, exothermic reaction.

The equation of kinetics for process (6.32) taking into account both forward and also reverse reactions can be written in the form

$$\frac{d\,XY}{dt} = k_1 XY\cdot WZ - k_2 XW\cdot YZ^{*}. \qquad (6.33)$$

Constants of reaction rates, depending only on temperature, are connected, as usual, by the principle of detailed balancing:

$$\frac{k_2}{k_1} = \frac{(XY)(WZ)}{(XW)(YZ)} = K(T). \qquad (6.34)$$

Using the ideas of the theory of collisions, for constants of reaction rates it is possible to write expressions consistent with the expression for rate of dissociation. Thus, if one were to consider for

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*Reactions in whose elementary event participate two molecules (atom), are called bimolecular in distinction from monomolecular reactions, in which occurs decomposition of one molecule into simpler ones or into atoms, for instance, XY → X + Y.

simplicity that in surmounting the potential barrier E only the component of translational energy of colliding particles along the line of their centers is effective, and other components, just as internal degrees of freedom of molecules, are ineffective in this ration, we will obtain

$$k_1 = P\sigma\bar{v}'e^{-\frac{E}{kT}}, \tag{6.35}$$

where P, as earlier, is the probability that as a result of a sufficiently energetic collision, chemical transformation indeed will occur (P is sometimes called the steric factor).

Experiment shows that many reactions, especially those in which complex molecules participate, occur much slower than it would have been possible to expect, proceeding from the number of sufficiently energetic collisions: probability P frequently turns out to be very small, even of the order of 10^{-8}.

A more defined estimate of the reaction rate in a number of cases can be obtained using the so-called method of activated or transition complex,* which consists of the following. Potential energy of the system of atoms participating in the elementary event of a reaction, depends on their mutual configuration. If change of coordinates of atoms occurs sufficiently slowly (and this is practically always so), the electron state of the system changes continuously, and potential energy depends only on nuclear coordinates (this corresponds to adiabatic approximation in the theory of

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*A detailed account of this method and its applications to calculation of speeds of a number of reactions can be found in [38]; see also [27].

molecules). Potential energy constitutes a continuous surface in the configurational space of nuclear coordinates. At initial and final configurations of atoms, potential energy is minimum. For instance, for reaction (6.32) energy is minimum when atoms are united in molecules XY + WZ and XW + YZ, while molecules are separated at large distance from each other.

In order that the reaction occur, the point describing motion of system in configurational space should pass through maximum, dividing minima on the surface, to surmount the potential barrier. There exist, in general, different paths from the initial state to the final. Actually the most profitable way of reaction is carried out, corresponding to least value of maximum of energy; the surface of energy near this path has the character of a "hollow." Figure 6.3 schematically depicts the cross section of surface of energy along the "bottom of the hollow," while path of reaction also corresponds to coordinate of decomposition.

The peak of the potential barrier corresponds to a very close approach of the reacting particles. In its neighborhood, in the region with linear dimensions δ of the order of molecular dimensions, atoms form something like a molecule. Such a state is called an activated complex. However, a fundamental distinction of the activated complex from the molecule is that a molecule is in a stable state with minimum of potential energy; the complex is in a state of unstable equilibrium with maximum of potential energy as a function of the coordinate of decomposition. The point describing the state of the system moves along reaction path with a speed of the order of speeds of relative motion of atoms, i.e., with average speed $\overline{v}$ of the order of thermal speed. The time of its stay in the neighborhood of the peaks i.e., life of the activated complex, is of the order $\tau = \delta/\overline{v}$. When $\delta \approx 10^{-8}$ cm and $\overline{v} \approx 10^4$ cm/sec $\tau \approx 10^{-12}$ sec. The life of a complex is very short as compared to the characteristic time of reaction (time of achievement of chemical equilibrium in mixture of gases). This serves as a base for the basic assumption of theory, which assumes that complexes, considered as some molecules which possess basically the usual thermodynamic properties, are in chemical equilibrium with reagents, and concentration of complexes "watches" after change of concentrations of reagents.*

If it is considered that every formed complex disintegrates in the direction of products of reaction, then the number of events of the reaction in 1 cm^3 in 1 sec equals the number of disintegrations of complexes, i.e., the number of complexes in 1 cm^3 divided by their life. Designating by chemical symbols A, B, M the number of reagents A and B and complexes M in 1 cm^3 (for instance, for reaction (6.32) A and B is XY and WZ, and M $\equiv$ XYWZ), we will find that the number of events of the forward reaction in 1 cm^3 in 1 sec equals $k_1 \cdot A \cdot B = M/\tau$, whence constant of rate of forward reaction is $k_1 = (M/AB)\ (1/\tau)$.

According to the law of active materials (see § 3 Ch. III) the ratio of numbers of particles participating in reaction $A + B \rightarrow M$, in the state of equilibrium is equal to the ratio of statistical sums of particles. (Inasmuch as by A, B, M are implied the numbers of particles in 1 cm^3, volumes V entering into translational sums should be set equal to 1 cm^3). Separating from statistical sums factors of the type exp $(-\varepsilon/kT)$, corresponding to zero-point energy of particles,

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*Really, relaxation time for the establishment of similar equilibrium is of the order of the life of the complexes, i.e., is very small.

and noticing that $\varepsilon_M - (\varepsilon_A + \varepsilon_B) = E$ equals activation energy, we will obtain

$$\frac{M}{AB} = \left(\frac{Z_M}{Z_A Z_B}\right) \exp\left(-\frac{E}{kT}\right).$$

Statistical sums Z_A, Z_B are calculated by the usual methods which concerns statistical sum of complex, then here it is necessary to note the following. The complex is stable as also a usual molecule, in relation to all changes of configuration of atoms, with the exception of direction along path of reaction. Therefore, if one were to consider normal vibrations of the complex, the frequency of normal vibration, corresponding to coordinate of decomposition has an imaginary value. If we assume that the peak of the potential barrier is sufficiently flat, then motion along coordinate of decomposition can be considered as translational with average speed $\overline{v}_x = (kT/2\pi m^*)^{1/2}$, where m* is effective mass of complex. The statistical sum of one-dimensional translational motion of a particle with mass m* on segment δ, equivalent to the "volume" occupied by complexes along coordinate of decomposition, equal to $Z_{\text{one dim. trans.}} = (2\pi m^* kT/h)^{1/2}\delta$. (cf. with formula (3.12)). During calculation of statistical sum of complex Z_M one should replace the statistical sum of one of the normal vibrations of this translational sum. Thus, constant of speed of reaction equals

$$k_1 = \frac{M}{AB}\frac{1}{\tau} = \frac{Z_M}{Z_A Z_B} e^{-\frac{E}{kT}} \frac{\overline{v}_x}{\delta} = \frac{Z_M^*}{Z_A Z_B} e^{-\frac{E}{kT}} \left(\frac{2\pi m^* kT}{h}\right)^{\frac{1}{2}} \delta \left(\frac{kT}{2\pi m^*}\right)^{\frac{1}{2}} \frac{1}{\delta},$$

where Z_M^* designates statistical sum of complex from which is excluded the factor corresponding to one normal vibration.* From this formula it is clear that indeterminate value δ and m* are reduced. Introducing still so-called transmission coefficient $\varkappa$ characterizing disintegration probability of complex in the direction of products of reaction (and not in the direction of initial particles; $\varkappa$ is usually of the order of unity, we will finally obtain the constant of reaction rate

$$k_1 = \varkappa \frac{kT}{h} \cdot \frac{Z_M^*}{Z_A Z_B} e^{-\frac{E}{kT}}. \tag{6.36}$$

The origin of the factor of dimension of frequency kT/h in universal for all reactions, (6.42) can be imagined thus. We will consider the degree of freedom of a complex along the reaction path as a normal vibration with frequency ν. Its statistical sum is equal to $kT/h\nu$ (when $h\nu < kT$), so that $Z_M = Z_M^* kT/h\nu$. But every vibration actually leads to disintegration of the complex, so that life τ is equal to period of vibrations $\tau = 1/\nu$, whence also is obtained $(kT/h\nu)1/\tau = kT/h$, i.e., formula (6.36).

Placing in (6.36) specific expressions for statistical sums and comparing the obtained formula with formula (6.35), the value of steric factor P can be obtained in evident form.

Let us consider first of all purely formally the imaginary reaction of unification of two atoms into a molecule without participation of a third particle. Then Z_A and Z_B are purely translational sums, and Z_M^* consists of translational and rotational (vibration of

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*It can be calculated by the usual methods if one defines the constants of the complex as "molecular."

diatomic complex is excluded). Putting in (6.36) $Z_{A,B} = (2\pi m_{A,B}kT/h^2)^{3/2}$, $Z_M^* = [2\pi(m_A + m_B)kT/h^2]^{3/2}\cdot(8\pi^2 IkT/h^2)$, and noticing that moment of inertia of complex $I = d_{12}^2 m_A m_B/(m_A + m_B)$, where d_{12} is the average diameter of atoms $d_{12} = (d_A + d_B)/2$, we will obtain exactly formula (6.35) of the theory of collisions, if one identifies steric factor P with transmissional coefficient $\varkappa$ (effective cross section of collisions $\sigma = \pi d_{12}^2$).

In general for an estimate it is convenient to write the statistical sums of reagents and complex in the form of products of sums, each of which corresponds to one degree of freedom and not to distinguish sums belonging to identical degrees of freedom but to various particles. For instance, if A and B are diatomic molecules, $Z_A \sim Z_B \sim Z_{\text{trans}}^3 Z_{\text{rot}}^2 Z_{\text{vib}}$. Assuming that the complex is nonlinear, we will write $Z_M^* \sim Z_{\text{trans}}^3 Z_{\text{rot}}^3 Z_{\text{vib}}^5$ (in complex 4 atom, 6 vibrational degrees of freedom, while one is excluded). Thus, in order of magnitude

$$k_1 \sim \varkappa \frac{kT}{h} \frac{Z_{\text{пост}}^3 Z_{\text{вращ}}^3 Z_{\text{кол}}^5}{Z_{\text{пост}}^6 Z_{\text{вращ}}^4 Z_{\text{кол}}^2} e^{-\frac{E}{kT}}.$$

Analogous to the reaction of unification of two atoms into a molecule, factor

$$\frac{kT}{h}\frac{Z_{\text{пост}}^3 Z_{\text{вращ}}^2}{Z_{\text{пост}}^6} \approx \frac{kT}{h}\frac{Z_{\text{вращ}}^2}{Z_{\text{пост}}^3} \approx \pi d_{12}\cdot\bar{v}'$$

gives approximately the number of collisions in (6.32), so that the steric factor in order of magnitude equals

$$P \sim \varkappa \frac{Z^{5}_{\text{кол}}}{Z^{3}_{\text{вращ}}}.$$

At room temperatures Z_{vib} has the order of unity. Z_{rot} of the order of 10-100, is less the lighter the molecule is. Hence it is clear that the steric factor can be a very small magnitude, 10^{-3}-10^{-6}.

In § 10 we will use the method of the activated complex to estimate rate of formation of nitrogen peroxide in heated air which is important for clarification of certain optical phenomena observed with a strong explosion.

§ 8. Oxidation Reaction of Nitrogen

In heating air to a temperature of several thousand degrees in it occurs the chemical reaction:

$$\frac{1}{2}N_2 + \frac{1}{2}O_2 + 21.4\,\frac{\text{kcal}}{\text{mole}} = NO, \qquad (6.37)$$

as a result of which will be formed a rather considerable quantity of nitric oxide NO. Equilibrium concentrations of oxide at temperatures of 3000-10,000°K and air densities of normal order reach several percent (see Table 3.1, in Ch. III). A certain quantity of oxide is oxidized to dioxide NO_2, whose equilibrium concentrations in the shown conditions have an order of 10^{-4} - 10^{-2}%. Oxides of nitrogen play an important role in radiation and absorption of light by heated air. Especially great in this ratio is the role of nitrogen peroxide in the region of temperatures of the order of 2000-4000°K, when optical properties of air in the visible part of the spectrum are practically wholly determined by NO_2 molecules. In heating air in strong shock waves, for instance during an explosion, temperature and air density undergo very rapid changes; therefore, in estimating concentrations of oxides of nitrogen there is an essential value in the question about kinetics of their formation and decomposition.

As will be shown in Chapter VIII, IX, features of kinetics determine certain characteristic optical effects observed during a strong explosion. In this section will be considered kinetics of the oxidation of nitrogen, and in the following — kinetics of oxidation of oxide to dioxide.

The oxidation reaction of nitrogen has a high energy of activation, therefore practically it occurs only at sufficiently high temperatures of the order of 2000°K and higher. The reaction was studied in detail both experimentally and also theoretically in the work of Ya. B. Zel'dovich, P. Ya. Sadovnikov, and D. A. Frank-Kamenetskiy [39].

In experiments the reactions of formation and decomposition of nitric oxide were studied with the help of explosive bombs in which a mixture of hydrogen and oxygen was burned. In such a way high temperatures of the order of 2000°K were obtained. To a mixture H_2 and O_2 were added nitrogen and, in different concentrations, nitric oxide. Upon small additions oxide was formed as a result of the combination of oxygen and nitrogen; with large additions, the initially introduced oxide was decomposed. After explosion residual quantities of oxide were determined and by means of comparison of theory with experiment reaction rates of formation and decomposition were found. The process itself of the combination of oxygen with hydrogen hardly affected the formation and disintegration oxide and served only as a means of obtaining a high temperature.

If one assumes that the reaction occurs according to a bimolecular mechanism, i.e., upon collision of two N_2 and O_2 molecules two molecules of NO are formed, then for the constant of the reaction rate it is possible to write a simple expression following from the theory of collisions (see formula (6.32)): $k' = P\bar{v}\sigma e^{-E/kT}$. By experiment was found the value of the pre-exponential factor, equal to $1.1 \cdot 10^3 O_2^{-1/2}$, where O_2 designated the number of molecules of oxygen in 1 cm^3. If one were to substitute, for instance, $O_2 = 10^{18}$ molecules/cm^3, we obtain a pre-exponential factor equal to $1.1 \cdot 10^{-6}$ cm^3/sec. When $T = 2500°K$ $\bar{v} \approx 2 \cdot 10^5$ cm/sec, $\sigma \approx 10^{-15}$ cm^2, for transition of probability P is obtained an improbably large value $P \approx 5000$. Thus, the assumption about bimolecular mechanism of reaction leads to a physically senseless result; experiment shows that in fact the reaction occurs much faster. N. N. Semenov expressed the assumption that the oxidation reaction of nitrogen occurs according to a chain mechanism in which an active role is played by free atoms of O and N:

$$O + N_2 \underset{k_2}{\overset{k_1}{\rightleftarrows}} NO + N - 75.5 \text{ kcal/mole,} \qquad (6.38)$$

$$N + O_2 \underset{k_4}{\overset{k_3}{\rightleftarrows}} NO + O + 32.5 \text{ kcal/mole.} \qquad (6.39)$$

Heats of reactions here correspond to energies of dissociation of molecules of N_2 and NO, equal to 9.74 ev = 225 kilocalorie/mole and

6.5 ev = 150 kilocalorie/mole.*

The rate of the process on the whole is determined first, by the endothermic reaction requiring an activation energy of not less than 75.5 kilocalorie/mole. As soon as resulting from the exchange $O + N_2 \rightarrow NO + N$ an atom of N is liberated, it immediately reacts with oxygen O_2, restoring the disappeared atom of O. Therefore, the concentration of O atoms in the reaction remains stationary and corresponds to equilibrium with O_2 molecules, which is established faster than the oxidation reaction of nitrogen occurs.**

Designating the constant of speeds as is done in formulas of (6.38), (6.39), we will write the general equations of kinetics:

$$\frac{dNO}{dt} k_1 \cdot O \cdot N_2 + k_2 \cdot N \cdot O_2 - k_3 \cdot N \cdot NO - k_4 \cdot O \cdot NO, \tag{6.40}$$

$$\frac{dO}{dt} = -\frac{dN}{dt} = -k_1 \cdot O \cdot N_2 + k_2 \cdot N \cdot NO + k_3 \cdot N \cdot O_2 - k_4 \cdot O \cdot NO. \tag{6.41}$$

In virtue of stationariness of the concentration of O we will equate the right side (6.41) to zero, will express the concentration of N through O, and will place the found expression in (6.40). We obtain

$$\frac{dNO}{dt} = 2 \frac{O}{k_2 \cdot O_2 + k_3 \cdot NO} (k_1 \cdot k_2 \cdot N_2 \cdot O_2 - k_3 \cdot k_4 \cdot NO^2). \tag{6.42}$$

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*In [39] the old values of energies of dissociation of N_2 and NO were accepted: 7.38 ev and 5.3 ev; however, as later to be mentioned calculations show (and also the most recent experiments [40]), new values of energies of dissociation do not contradict the assumption about chain mechanism. All numerical values of constants in the subsequent account correspond to new energies of dissociation.

**Inasmuch as atoms of oxygen are in equilibrium with O_2 molecules, the mechanism of dissociation of O_2 does not affect occurrence of the oxidation of nitrogen.

Let us make certain transformations. Constants k_3 and k_2 determine rates of exothermic reactions of an atom with a molecule and, probably, of one order. Inasmuch as the concentration of $NO \ll O_2$, the term $k_3 \cdot NO$ in the denominator (6.42) can be disregarded. The concentration of O atoms we express using equilibrium constant $O_2 \rightleftarrows 2O$, which we will designate C_0:

$$O = C_0\sqrt{O_2} = 6.6\cdot 10^{13} e^{-\frac{61\,000}{RT}}\sqrt{O_2}. \qquad (6.43)$$

Here, as also subsequently, all numerical values of constants of equilibrium and constants of reaction rates correspond to measurement of concentrations in units of molecules/cm^3. Energies are expressed in cal/mole. Gas constant R = 2 cal/mole·deg. Constants of rates are connected by the principle of detailed balancing, and namely:*

$$C_1 = \frac{(NO)(N)}{(N_2)(O)} = \frac{k_1}{k_3} = \frac{32}{9} e^{-\frac{75\,500}{RT}};$$

$$C_2 = \frac{(NO)(O)}{(O_2)(N)} = \frac{k_2}{k_4} = 6\cdot e^{\frac{32\,500}{RT}}.$$

Hence follows the indentity:

$$C_1C_2 = \frac{k_1k_2}{k_3k_4} = \frac{(NO)^2}{(N_2)(O_2)} = C^2 = \frac{64}{3} e^{-\frac{43\,000}{RT}}. \qquad (6.44)$$

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*Pre-exponential factors in equilibrium constants C_1, C_2, C are calculated in approximation of equality of masses N and O, of moments of inertia and frequencies N_2, O_2, NO during calculation of different symmetry and multiplicity of terms. This approximation is sufficiently accurate.

Removing k_3k_4 from parenthesis in (6.42) and using (6.44), we will obtain finally the equation of kinetics of the oxidation of nitrogen:

$$\frac{d\,NO}{dt} = k' \cdot N_2 \cdot O_2 - k \cdot NO^2 = k\{(NO)^2 - NO^2\}, \tag{6.45}$$

where constants of speeds equal

$$k' = \frac{2C_0k_1}{\sqrt{O_2}}, \quad k = \frac{k'}{C^2} = \frac{2C_0k_1}{C^2\sqrt{O_2}}. \tag{6.46}$$

Equation (6.45) differs from the usual equation of a bimolecular reaction by the dependence of constants of speed on the concentration of one of the reagents – oxygen.

The physical meaning of the expression for formation rate oxide $k' \cdot N_2 \cdot O_2 = 2C_0k_1N_2 \cdot \sqrt{O_2}$ is very simple: $C_0\sqrt{O_2}$ is the concentration of atomic oxygen, $k_1C_0\sqrt{O_2} \cdot N_2$ is the rate of the first reaction of the chain; but in virtue of the exothermic nature the second reaction follows "instantly" after the first, so that every event of the first reaction, which "conducts" the process, leads to the formation of two NO molecules.

Removing in constant of speed k_1 the factor $e^{-E_1/RT}$ and noticing that according to (6.43) $C_0 \sim e^{-61000/RT}$, it is possible to see that the activation energy for the reaction of formation of nitric oxide $E'(k' \sim e^{-E'/RT})$ is comprised of energy necessary on formation of one atom of oxygen – 61 kilocalorie/mole* and activation energy for the reaction of an atom of oxygen with a molecule of nitrogen – E_1.

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*This magnitude is effective for temperatures of the order of 2000-5000°; it differs somewhat from the energy of formation at absolute zero – 58.5 kilocalorie/mole.

In experiments described in [39], nitric oxide was obtained as a result of explosions of a fuel mixture containing oxygen and nitrogen. The quantity of oxide formed was measured after cooling of the explosion products. On the basis of theoretical consideration of kinetics of the reaction in the cooling process were removed activation energy of formation of the oxide E' = 125 ± 10 kilocalorie/mole and absolute value of constant of rate in the investigated interval of temperatures 2000-3000°K, where it is noted that more probable is an upper value of activation energy E' = 125 + 10 = 135 kilocalorie/mole. Hence, for activation energy of the first reaction of chain $O + N_2 \rightarrow NO + N$ is obtained the value $E_1 = 135 - 61 = 74$ kilocalorie/mole, coinciding with heat of endothermic reaction. This means that the reverse reaction $N + NO \rightarrow O + N_2$ occurs practically without activation (or with very small activation energy) which is typical for an exothermic reaction of a free atom with a molecule. Absolute values of constants of rate, which follow from experimental data, equal

$$k' = \frac{1.1\cdot 10^8}{\sqrt{O_2}} e^{-\frac{135\,000}{RT}}, \quad k = \frac{53}{\sqrt{O_2}} e^{-\frac{92\,000}{RT}} \frac{cm^3}{sec};\ O_2\,\frac{1}{cm^3}. \qquad (6.47)$$

Constant of rate for first reaction of chain $k_1 = 8.3\cdot 10^{-11} e^{-74000/RT}$. Comparison of this magnitude with formula (6.32) of the theory of collisions gives steric factor P = 0.086 (if one takes effective diameter $d_{12} = 3.75\cdot 10^{-8}$ cm equal to the diameter of a molecule of N_2, determined from data on viscosity). Such a value of P is fully reasonable.

Later investigation of the kinetics of formation of nitric oxide was undertaken by Glick and others [40], using a shock tube in which a gas mixture containing nitrogen and oxygen was heated by a shock wave to a temperature of 2000-3000°K. These authors found activation energy $E' = 135 \pm 5$ kilocalorie/mole ($E_1 = 74 \pm 5$ kilocalorie/mole) which agrees well with data of [39] and confirms coincidence of activation energy of the first reaction of chain E_1 with heat of reaction. Absolute values of the constant of rate also turned out to be close to data of the first work.

From formula (6.47) it is clear that activation energy for decomposition of nitric oxide is also very great, $E = E' - 43 = 92$ kilocalorie/mole; therefore, at low temperatures the oxide is decomposed very slowly. Owing to this during fast cooling of initially heated air the nitric oxide formed in it at high temperatures is kept after cooling for long time so that its concentration considerably exceeds equilibrium values which are very small at low temperatures (this effect carries the name of the effect of hardening; we will return to it in § 5 Ch. VIII). As can be seen from the equation of kinetics (6.45) and formulas (6.44), (6.47), the relaxation time for establishment of equilibrium concentration oxide is equal to:

$$\tau = \frac{1}{2K(\mathrm{NO})} = \frac{0.95\cdot 10^{-8}\sqrt{\mathrm{O}_2}}{(\mathrm{NO})} e^{\frac{92\,000}{RT}} = \frac{2.06\cdot 10^{-3}}{\sqrt{\mathrm{N}_2}} e^{\frac{113\,500}{RT}} \text{ sec} \qquad (6.48)$$

It decreases rapidly with an increase of temperature. Let us give

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*According to determination of time of relaxation (6.2), with a small distinction of NO from (NO), $\{(\mathrm{NO})^2 - \mathrm{NO}^2\} \approx 2(\mathrm{NO})\cdot\{(\mathrm{NO}) - \mathrm{NO}\}$, whence is obtained (6.48). Time τ characterizes not only approach to equilibrium, but also in general, the process of establishment of equilibrium, even if in the initial moment there was no oxide.

several values for air of normal density ($N_2 = 2.1 \cdot 10^{19}$ molecules/cm^3):

T, °K	1000	1700	2000	2300	2600	3000	4000
τ, sec	$2.2 \cdot 10^{12}$	140	1	$5.3 \cdot 10^{-3}$	$1.4 \cdot 10^{-3}$	$7.8 \cdot 10^{-5}$	$7.2 \cdot 10^{-7}$

§ 9. Rate of Formation of Nitrogen Peroxide at High Temperatures

The reaction of formation of nitrogen peroxide from oxide

$$2NO + O_2 = 2NO_2 + 25.6 \text{ kcal/mole} \qquad (6.49)$$

is exothermic, therefore the lower the temperature is, all the more so does equilibrium shift in the direction of oxidation of oxide. This reaction is widely used in industry and is well studied experimentally at temperatures lower than 1000°K. It has very small, practically inconspicuous, activation energy and therefore occurs easily at normal temperatures. The equation of kinetics of the reaction has the form

$$\frac{dNO_2}{dt} = 2\{k_1' NO^2 \cdot O_2 - k_2' NO_2^2\} = 2k_2'\{(NO_2)^2 - NO_2^2\}. \qquad (6.50)$$

Constants of reaction rates describe number of events of reactions; the factor 2 considers the fact that in every event are formed or disappear two NO_2 molecules. Relaxation time for establishment of chemical equilibrium of nitrogen peroxide with oxide and oxygen equals

$$\tau' = \frac{1}{4k_2'(NO_2)} = \frac{C^2}{4k_1'(NO_2)}, \qquad (6.51)$$

where $C^2 = (NO_2)^2/NO^2 \cdot O_2$ is the equilibrium constant of dioxide with actual quantities oxide and oxygen, which can be also unbalanced. The equilibrium constant can be calculated by the statistical method. After substitution of values of all parameters it turns out to equal*

$$C=\frac{(NO_2)}{NO\cdot O_2^{\frac{1}{2}}}=\frac{1{,}25\cdot 10^{-11}}{T^{\frac{3}{4}}}\frac{\left(1-e^{-\frac{2740}{T}}\right)\left(1-e^{-\frac{2270}{T}}\right)^{\frac{1}{2}}e^{\frac{6460}{T}}}{\left(1+e^{-\frac{174}{T}}\right)\left(1-e^{-\frac{916}{T}}\right)\left(1-e^{-\frac{1960}{T}}\right)\left(1-e^{-\frac{2310}{T}}\right)}, \qquad (6.52)$$

where temperature is everywhere expressed in degrees, and dimension C corresponds to measurement of concentrations in numbers of particles in 1 cm^3.

Constant of speed k_1' was calculated in [38] by the method of the activated complex, where good agreement was obtained with experimental data of Bodenstein [44], investigating reaction rate in an interval of temperatures from 353° to 845°K. Comparison testifies to the absence of activation energy for reaction. The formula for constant of speed k_1', derived in [38], can be used to estimate rate and time of relaxation also at high temperatures, which by experiment were not studied. Results of calculation of time of relaxation of formation of nitrogen peroxide in heated air for several values of temperature and densities are presented in Table 6.3 (here equilibrium concentrations (NO_2) were calculated on the basis of equilibrium values of concentrations of oxide (NO) and oxygen (O_2).

At high temperatures and especially with low densities of gas

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*As was noted by one of the authors [41], the equilibrium constant given in a widely-popularized reference book [42], is taken from an erroneous work [43] and is oversized by 2.42 times.

Table 6.3. Relaxation Times for Establishment of Equilibrium Concentration of Nitrogen Peroxide in Air, in Sec. (τ' – trimolecular reaction, τ'' – bimolecular)

T, °K	ρ/ρ_{nor}					
	10		5		1	
	τ'	τ''	τ'	τ''	τ'	τ''
1600			$8\cdot10^{-3}$	0.35	0.09	0.69
1800			$3.5\cdot10^{-3}$	$3.9\cdot10^{-2}$	0,04	0.09
2000	$6.75\cdot10^{-4}$	$3.1\cdot10^{-3}$	$1.95\cdot10^{-3}$	$4.5\cdot10^{-3}$	$2.2\cdot10^{-2}$	0.01
2300	$1.42\cdot10^{-4}$	$2.7\cdot10^{-4}$	$4\cdot10^{-4}$	$4.0\cdot10^{-4}$	$4.5\cdot10^{-3}$	$0.9\cdot10^{-3}$
2600	$4.75\cdot10^{-5}$	$4.4\cdot10^{-5}$	$1.35\cdot10^{-4}$	$6.3\cdot10^{-5}$	$1.5\cdot10^{-3}$	$1.4\cdot10^{-4}$
3000	$1.75\cdot10^{-5}$	$6.6\cdot10^{-6}$	$4.75\cdot10^{-5}$	$9.4\cdot10^{-6}$	$5.5\cdot10^{-4}$	$2.1\cdot10^{-5}$
4000	$2.5\cdot10^{-5}$	$2.8\cdot10^{-7}$	$7.5\cdot10^{-6}$	$4.0\cdot10^{-7}$	$1.05\cdot10^{-6}$	$1.0\cdot10^{-6}$

with a trimolecular reaction (6.49) competes another mechanism of formation of dioxide

$$NO + O_2 + 45\,\frac{\text{kcal}}{\text{mole}} = NO_2 + O. \qquad (6.53)$$

In spite of the fact that this reaction is endothermic, it possesses as compared to reaction (6.49) the same advantage that is carried out by means of not triple, but paired collisions of molecules. This advantage should appear at high temperatures, when conditions for activations are favorable. Reaction (6.53) was not studied by experiment; a theoretical estimate of its rate was given in the work of one of the authors [41].

The equation of kinetics for reaction (6.53) may be written in the form

$$\frac{d\,NO_2}{dt} = k_1'\cdot NO\cdot O_2 - k_2' NO_2\cdot O = k_2'\cdot O\{(NO_2) - NO_2\}. \qquad (6.54)$$

Relaxation time:

$$\tau'' = \frac{1}{k_2'\cdot O}. \qquad (6.55)$$

Let us estimate the constant of rate by the method of the activated complex, the essence of which was presented in § 7. In particular, this estimate can serve as an illustration of a specific application of the method. For convenience we will consider reverse reaction $NO_2 + O \rightarrow NO_3^* \rightarrow NO + O_2$, where the asterisk marks a complex. According to general formula (6.36) constant of rate k_2'' equals:

$$k_2'' = \varkappa \frac{kT}{h} \frac{Z^*_{NO_3}}{Z_{NO_2} \cdot Z_O}.$$

Calculation of statistical sums of O atoms and NO_2 molecules does not present difficulties, since spectroscopic constants of the NO_2 molecule are known. Regarding, however, a complex, then here is a whole series of unknowns of magnitudes, which for an estimation must be selected wisely.

The mass of an NO_3^* complex is 1.39 times more than the mass of an NO_2 molecule. Assuming that its dimensions somewhat exceed the dimensions of a molecule of NO_2, we will consider that the average moment of inertia of the complex is 1.5 times more than the average moment of inertia of a molecule of NO_2. The natural frequencies of a molecule of NO_3, with respect to which it would have been possible to judge about frequencies of complex, are unknown. It is possible to trust that the three highest frequencies are less than the frequencies of a NO_2 molecule: $h\nu_{NO_2}/k = 960, 1960, 2310^{\circ}K$, since the bonding in a complex is weaker. It is easy to check that at temperatures of $2000\text{-}4000^{\circ}$ the constant of rate is not very sensitive to selection of frequencies of complex within the limits of a reasonable interval. Let us set for calculation the following five frequencies $h\nu^*/k = 600, 800, 900, 1500, 2000^\circ K$ (the sixth is excluded from Z^*). The complex is asymmetric, so that factor of symmetry $\sigma = 1$. Statistical weight of electron state $g^* > 2$, since the complex contains one unbound electron. Let us set $g^* = 2$. Activation energy of the exothermic reaction $NO_2 + O \rightarrow NO + O_2$, apparently, is minute, as occurs when one of the reagents is a free atom. Let us set for estimation E = 10 kilocalorie/mole; this in the worst case can underestimate rate of reaction by 2-3 times at temperatures of 2000-4000°.

Putting these, and also other known constants in expressions of statistical sums and taking transmissional coefficient $\varkappa$ equal to one, we will obtain constant of speed

$$k_2 = \frac{1{,}16\cdot 10^{-13}}{\sqrt{T}} \frac{\prod_{i=1}^{5} Z^{*}_{\text{кол}\, i}}{\prod_{i=1}^{3} Z_{\text{кол}\, NO_2\, i}} e^{-\frac{5030}{T}} \text{ cm}^3/\text{sec} \qquad (6.56)$$

where vibrational statistical sums equal $Z_{vib} = (1 - e^{h\nu/kT})$. Using the theory of collisions (see formula (6.35)) in order to obtain, the constant of rate of the same order as according to formula (6.56), one should have considered steric factor P of a magnitude of the order of $2 \cdot 10^{-4}$. To select so small a value without any visible bases would be fairly difficult, so that the theory of collisions in this case turns out to be practically useless and estimation of reaction rate is possible only using the method of the activated complex.

Relaxation times calculated for air by the formulas (6.55), (6.56) also are presented in Table 6.3.

Comparison of these times shows that for air densities of an order less than normal and temperatures ~2000-3000°K second reaction occurs faster and is basic.

2. Ionization and Electron Excitation

§ 10. Basic Mechanisms

Excitation of the highest electron states of atoms (molecules, ions) and ionization have much in common. In essence, ionization constitutes the limit case of electron excitation, when an electron bound to an atom obtains energy sufficient for breakaway from the atom and transition into a continuous spectrum. Each of the elementary processes, as a result of which occurs excitation of electrons in atoms, can also lead to ionization, if for this it siezes energy. Therefore, it is convenient to classify and to consider elementary processes uniting ionization and excitation.

All elementary processes of excitation and ionization can be subdivided into two categories: excitation and ionization of atoms (molecules, ions) impacts of particles and photoprocesses, in which the role of one of the "particles" is played by light quantum. In the first circle of processes one should distinguish ionization and excitation by electron impact and nonelastic collisions of heavy particles, since the probabilities of those and other nonelastic collisions sharply differ from each other. According to such classification the basic reactions of ionization can be written in the following symbolic form (A, B — heavy particles, e — electrons, $h\nu$ — light quanta):

$$A + e = A^* + e + e, \qquad (6.57)$$

$$A + B = A^* + B + e, \qquad (6.58)$$

$$A + h\nu = A^* + e. \qquad (6.59)$$

The reverse processes proceeding from right to left, lead to recombination of electrons with ions: the first two constitute recombination in triple collisions with participation of an electron or a heavy particle as the third particle; the last reaction is photo-recombination or photo-capture of electrons.

To each of the processes of (6.57)-(6.59) corresponds the process of excitation (the excited atom is marked by an asterisk):

$$A + e = A^* + e, \qquad (6.60)$$

$$A + B = A^* + B, \qquad (6.61)$$

$$A + h\nu = A^*. \qquad (6.62)$$

The first two reverse processes constitute deactivation of excited atoms by so-called impacts of a second kind; the third is luminiscence of an excited atom.

In general, processes of all three types occur in gas simultaneously. However, frequently one of the processes turns out to be predominant. With energies of the order of excitation potentials or ionization of atoms, i.e., an order of several or ten electron volts, effective cross sections of nonelastic collisions of heavy particles are several orders less than effective cross sections of nonelastic electron impacts. Furthermore, velocities of heavy particles with comparable energies is approximately a hundred times less than velocities of electrons (with respect to square root of masses). Therefore, processes of the type of (6.58), (6.61) in heated gas have a value only if there are practically no free electrons. For degrees of ionization of the order of 10^{-5}-10^{-4} and higher, rates of processes of the first type (6.57), (6.60) are larger than rates of processes with participation of heavy particles and the role of the latter is negligible. Essentially, ionization by impacts of atoms or molecules is important only for formation of a small initial quantity of "initiating" electrons, when gas is "instantaneously" heated, as happens, for instance, during the passage of a strong shock wave. In certain cases initial ionization in "instantly" heated gas is created by a sufficiently intense radiation flux or fast electrons arriving from without, from earlier heated regions, and thereby even this "initiating" role of the second process is brought to zero.

The comparative role of the first and third processes in a more complicated way depends on macroscopic conditions. The number of events of ionization by electron impact in 1 sec in 1 cm^{-3} is proportional to density of electrons, whereas the number of events of photo-ionization is proportional to density of radiation.

If dimensions of the region occupied by heated gas are sufficiently great as compared to paths of quanta, so that density of radiation is considerable and of the order of equilibrium, it does not depend on density of gas and is determined only by temperature. Therefore, in sufficiently rarefied gas rate of ionization by electron impact turns out to be small and a basic role is played by photoionization. The same pertains also to the processes of excitation, and also to the reverse processes of recombination and deactivation: photo-recombination predominates above recombination in three-body collisions, and luminiscence of excited atoms predominates above removal of excitation by impacts of the second kind. Such a position is observed, for instance, in stellar photo-spheres.

If the region occupied by heated gas, is bound and transparent ("optically is thin"), quanta radiated in the gas, not being held back, abandon the heated volume, and density of radiation in gas is less than equilibrium. In these conditions even with a low density of electrons the rate of ionization by electron impact can turn out to be higher than rates of photo-ionization whereas relationship of rates of reverse processes of recombination can remain as before, i.e., photo-recombination can predominate.

In a sufficiently dense gas photo-ionization and photo-recombination play a secondary role as compared to the first process (6.57). Speaking of reactions of ionization (6.57)-(6.59), one should consider that not only atoms remaining in the ground state, but also excited atoms can be ionized, so that to the list of reactions (6.57)-(6.59) one should also add reactions of the type

$$A^* + e = A^* + e + e, \qquad (6.63)$$

$$A^* + B = A^* + B + e, \qquad (6.64)$$

$$A^* + h\nu = A^* + e. \qquad (6.65)$$

The same pertains also to processes of excitation (6.60)-(6.62), more exactly, to processes of increase of degree of excitation. In spite of the fact that the number of excited atoms is usually considerably less than the number of atoms remaining in the ground state, the role of ionization of excited atoms in releasing electrons, is not small, in any case not exponentially small, since correspondingly in their ionization participate particles with smaller energies. Really, the number of particles able to ionize an unexcited atom is proportional to $\exp(-I/kT)$, where I is ionization potential. But the number of events of ionization of atoms excited to level E^*, also is proportional to $e^{-E^*/kT}\, e^{-(I-E^*)/kT} = e^{-I/kT}$, since to the first factor is proportional the number of excited atoms, and to the second — the number of particles able to ionize an atom. (Usually in not too dense a gas ionization occurs when $kT \ll I$, so that $I/kT \gg 1$ and Boltzmann factor $e^{-I/kT}$ is very significant).

The comparative role of ionization of excited and unexcited atoms in conditions of equilibrium excitation is determined, mainly, by effective cross sections of ionization of those and others during impacts by particles with energy which is above threshold energy.

In molecular gas in which the molecules and atoms possess potentials of ionization not considerably exceeding energy of dissociation, ionization starts long before the end of dissociation, so that there exists a region of temperatures in which simultaneously concentration of electrons and concentration of molecules are considerable. An example is air at temperatures of the order of 7000--15,000°K – very important from the point of view of practical application. In this case, along with the shown processes of ionization (6.57)-(6.59), there exist more complicated processes, the most important of which is recombination of atoms into a molecule with simultaneous ionization.

This process from the viewpoint of energy profitably differs from others by the fact that it requires an energy consumption which is smaller than the ionization potential by the magnitude of the released energy of dissociation. At comparatively low temperatures and small degree of ionization the most important role for ionization of air is played by the reaction:

$$N + O + 2.8\ \mathrm{ev} = NO^{*} + e, \qquad (6.66)$$

which occurs several orders faster than simple ionization of NO by the impacts of atoms and molecules.* In recombination of electrons with ions in molecular gases an important role is played by so-called dissociative recombination. In particular, in air occur the processes

$$\begin{aligned} e + O_2^* &\rightarrow O^* + O^* + 6.9 \text{ ev}, \\ e + N_2^* &\rightarrow N^* + N^* + 5.8 \text{ ev}, \\ e + NO^* &\rightarrow N^* + O^* + 2.8 \text{ ev}. \end{aligned} \qquad (6.67)$$

As a result of dissociative recombination excited atoms are formed. The released binding energy of an electron is expended on dissociation of the molecule, and the surplus goes to excitation of atoms and partially passes into kinetic energy.

If in gas there are atoms or molecules possessing an electron affinity (for instance, H, O, O_2, Cl, Br, I., and others), at comparatively low temperatures negative ions are formed which renders an essential influence on kinetics of formation and disappearance of free electrons. Besides reactions of the type (6.57)-(6.59), in which A and A^+ are replaced correspondingly by A^- and A, more complicated energetically advantageous reactions of the type (6.66) can occur; for instance in air — it is exothermic reactions:

$$\begin{aligned} N + O^- &= NO + e + 4 \text{ ev}, \\ O + O^- &= O_2 = e = 3.6 \text{ ev}. \end{aligned} \qquad (6.68)$$

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*At comparatively low temperatures the basic supplier of free electrons in air is NO molecules, whose ionization potential $I_{NO} =$ $= 9.25$ ev lower than for all other components of air ($I_{O_2} = 12.15$ ev, $I_{N_2} = 15.56$ ev, $I_O = 13.57$ ev, $I_N = 14.6$ ev, $I_{Ar} = 15.8$ ev).

A full list of reactions occuring in heated air and leading to formation and disappearance of free electrons, and also to exchange by a charge, with indication of their power yield, is in [73].

§ 11. Ionization by Electron Impact

Let us consider the process of first ionization of gas from identical atoms and estimate characteristic time for first reaction (6.57) on the assumption that all atoms are ionized from the ground state, and during recombination an electron is captured on the ground level. The effective cross section of ionization during collisions depends on relative speed of colliding particles. Inasmuch as the velocity of atoms at comparable temperatures of atoms and electrons is always considerably less than velocity of electrons, relative velocity coincides with the latter; the reduced mass characterizing kinetic energy of relative motion coincides with mass of electron.

If N_a and N_e are the numbers of atoms and electrons in 1 cm^3, $f_e(v)dv$ is the function of Maxwellian distribution of electrons with respect to velocities, corresponding to electron temperature T_e*, $\left(\int\limits_0^\infty f_e(v)dv = 1\right)$ and $\sigma_e(v)$ is effective cross section of ionization by electron impact, then the number of events of ionization in 1 cm^3 in 1 sec equals

$$N_a N_e \int\limits_{v_k}^{\infty} \sigma_e(v)\, v f_e(v)\, dv = N_a N_e \alpha_e, \qquad (6.69)$$

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*Due to the large difference of masses of electrons and atoms exchange of energies between electrons and heavy particles during elastic collisions occurs rather slowly. Therefore, electron temperature, in general, can differ from translational temperature of heavy particles (see § 14).

where integration spreads according to velocities of electrons, whose energy exceeds ionization potential: $m_e v_k^2/2 = I$.

Designating constant of recombination rate by β_e,* we will write the equation of kinetics of the first reaction (6.57):

$$\frac{dN_e}{dt} = \alpha_e N_a N_e - \beta_e N_+ N_e^2, \qquad (6.70)$$

where the number of ions N_+ equals number of electrons N_e. Constants of velocities α_e and β_e are connected by the principle of detailed balancing:

$$\beta_e = \frac{\alpha_e}{K(T_e)}, \qquad (6.71)$$

where the equilibrium constant is determined by Saha formula (3.44):

$$K(T_e) = \frac{(N_e)(N_+)}{(N_a)} = \frac{g_+}{g_a} \frac{2(2\pi m_e kT_e)}{h^2}^{\frac{3}{2}} e^{-\frac{I}{kT_e}} = 4.85 \cdot 10^{15} \frac{g_+}{g_a} T^{\circ\frac{3}{2}} e^{-\frac{I}{kT}} 1/cm^3. \qquad (6.72)$$

The number of recombinations in 1 cm^3 in 1 sec is sometimes written in the form $Z_{rec} = b_e N_+ N_e$. The magnitude $b_e = \beta_e N_e$ is called coefficient of recombination. b_e has a dimension in cm^3 sec, the same as constant of rate of ionization α_e.

If concentration of electrons (and ions) is much less than equilibrium, recombination does not play a role and the development of ionization by electron impact carries the character of an electron avalanche: if it is considered that electron temperature does not

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*We will not extract the integral expression for recombination rate, similar to (6.69).

depend on time, concentration of electrons exponentially grows in time $N_e = N_e^0 \exp(t/\tau_e)$; here N_e^0 is the "initial" number of electrons, and the scale of time of build-up of avalanche approximately ($N_a \approx$ const) equals:

$$\tau_e = \frac{1}{\alpha_e N_a}\,^{*}. \qquad (6.73)$$

It is easy to check that magnitude τ_e characterizes also relaxation time for approach to ionization equilibrium by means of first mechanism (6.57). More exactly, when $|(N_e) - N_e| \ll (N_e)$, relaxation time, according to general determination (6.2), is twice less than τ_e.

The typical curve of dependence of effective cross section of ionization σ_e on speed or energy of electrons is depicted in Fig. 6.4.

The cross section increases after the threshold of ionization $\varepsilon_e = I$, attains maximum when energy of electrons is a few times more than threshold energy, and then slowly drops. In maximum the cross section, as a rule, is of the order of 10^{-16} cm^2. In not too dense a gas ionization sets in usually at temperatures of much smaller

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*It is necessary to stress that the simple exponential law of build-up of electron avalanche with scale of time τ_e is accurate only under the condition that T_e = const. In real conditions electron temperature can actually depend on time. The fact is that when $kT_e \ll I$ a very great fraction of thermal energy of electrons is expended on ionization: roughly speaking, on the production of one new electron is expended a thermal energy of I/kT_e electrons. If there is no source to replenish loss of energy of electron gas on ionization, the electron temperature drops with time, $\alpha_e \sim \exp(-I/kT_e)$ sharply decreases, development of avalanche fades. At the front of a shock wave losses of energy of electrons are replenished owing to flux of energy from atoms (ions) to electrons. For in greater detail, see § 10 Ch. VII.

ionization potential: $I/kT_e \gg 1$. Thus, for instance, in atomic hydrogen when $N_a = 10^{19}$ 1/cm^3 (which corresponds to a pressure of undissociated molecular hydrogen at room temperature, equal to 135 mm Hg) and $T = 10{,}000^\circ$K the equilibrium degree of ionization is equal to $6.25 \cdot 10^{-3}$; now $I/kT = 15.7$.

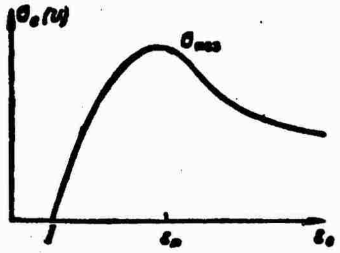

Fig. 6.4. Dependence of effective cross section of ionization by electron impact on energy of the electron.

Energy sufficient for ionization is possessed only by electrons corresponding to the tail of Maxwellian distribution with respect to velocities, the number of which is exponentially small (proportional to $\exp(-m_e v^2/2kT_e) \ll 1$). Therefore, in integral (6.69) a basic role is played by electrons whose energy only somewhat, by a magnitude of the order kT_e ($kT_e \ll I$), exceeds the ionization potential. Theory and experiment show that near the threshold the effective cross section linearly depends on energy of electrons ε_e:

$$\sigma_e(v) \approx C(\varepsilon_e - I), \; C = \text{const.} \tag{6.74}$$

Putting this magnitude in expression (6.69) and integrating, we will find constant of ionization rate:

$$\alpha_e = \int_{v_I}^{\infty} \sigma_e(v) v f_e(v)\, dv = \sigma_e \cdot \bar{v}_e \left(\frac{I}{kT_e} + 2\right) e^{-\frac{I}{kT_e}}, \tag{6.75}$$

where

$$\bar{v}_e = \left(\frac{8kT_e}{\pi m_e}\right)^{\frac{1}{2}} = 6.21 \cdot 10^5 \sqrt{T_e}\ \text{cm/sec} \tag{6.76}$$

*is average thermal velocity of electrons, and σ_e is certain mean value of effective cross section σ_e (v), which accurately corresponds to energy of electrons $\varepsilon_e = I + kT_e$; $\sigma_e = CkT_e$.

Constant of recombination rate, according to (6.71), (6.72) and (6.75), equals

$$\beta_e = \frac{g_a}{g_+}\left(\frac{I}{kT_e}+2\right)\frac{h^3\sigma_e}{2\pi^2 m_e^2 kT} = \frac{g_a}{g_+}\left(\frac{I}{kT_e}+2\right)\frac{1.28\cdot 10^{-10}}{T_e^0}\,\sigma_e\,\text{см}^6/\text{sec} \qquad (6.77)$$

In not too dense a gas, when $I/kT_e \gg 1$, $\beta_e \sim T_e^{-1}(\sigma_e \sim T_e)$, characteristic time τ_e in region of small degrees of ionization depends on temperature according to the law $\tau_e \sim \exp(I/kT_e)$.

Table 6.4. Ionization by Electron Impact

Atom, molecule	I, ev	$C\cdot 10^{17}$ см²/ev	Region of applicability, ev	ε_{max}, ev	$\sigma_{e\,max}\cdot 10^{16}$ см²	Literature
H_2	15.4	0.59	16–25	70	1.1	[46]
He	24.5	0.13	24.5–35	100	0.34	[46]
N	14.6	0.59	15–30	~ 100	~ 2.1	[47]
N_2	15.6	0.85	16–30	110	3.1	[46]
O	13.6	0.6	14–25	~ 80	~ 1.5	[48]
O_2	12.1	0.68	13–40	110		[46]
NO	9.3	0.82	10–20	~ 100	3.25	[49]
Ar	15.8	2.0	15–25	100	3.7	[46]
		1.7	15–18			
Ne	21.5	0.16	21.5–40	~ 160	0.85	[46]
Hg	10.4	7.9	10.5–13	42	5.4	[46]
Hg		2.7	10.5–28			

In Table 6.4 are experimental data on cross sections of ionization of certain atoms and molecules by electron impact (for designations see in Fig 6.4).** The numerical value of constant C

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*Translation editor's note: Designation omitted from phrase in original; probably is $\bar{v}_e$.

**A detailed survey and analysis of source material is in the book of Messi and Barkhop [45]. We recommend also the book of V. L. Granovskiy [46].

coincides with effective cross section (in cm^2) for an energy of electrons exceeding ionization potential by 1 ev, i.e., with mean cross section σ_e at a temperature $T_e = 1$ ev $= 11{,}600^\circ K$, exactly characteristic for region of first ionization. As can be seen from the table, cross section σ_e has an order of 10^{-17} cm^2.

In order to obtain an idea about order of magnitudes, we will consider a specific example: argon when $T_e = 13{,}000^\circ K$ and $N_a = 1.7 \times 10^{-18}$ cm^{-3} (such density corresponds to a pressure of 50 mm Hg at normal temperature). Equilibrium degree of ionization in such conditions equals 0.14; $\sigma_e = 2.24 \cdot 10^{-17}$ cm^2; $\overline{v}_e = 7.1 \cdot 10^7$ cm/sec; constants of velocities: $\alpha_e = 2.10^{-14}$ cm^3/sec; $\beta_e = 5.9 \cdot 10^{-31}$ cm^6/sec, characteristic time $\tau_e = 2.9 \cdot 10^{-5}$ sec. At temperature $T_e = 16{,}000^\circ K$ and the same density time τ_e is approximately 15 times less: $\tau_e = 2 \cdot 10^{-6}$ sec.

§ 12. Excitation of Atoms by Electron Impact

Analogously to the preceding we will for simplicity consider that an atom possesses only one level E*, so that an atom is excited only as a result of transition from the ground state. Let us write the equation of kinetics of excitation:

$$\frac{dN^*}{dt} = \alpha_e^* N_a N_e - \beta_e^* N^* N_e. \qquad (6.78)$$

α_e^* is the constant of rate of excitation, and β_e^* is the constant of the deactivation rate, equal to $\beta_e^* = \overline{v}_e \cdot \sigma_{e2}$, where σ_{e2} is effective cross section averaged according to Maxwellian distribution for electron impact of the second kind. Constant of rate of excitation is expressed through effective cross section of excitation $\sigma_e^*(v)$

precisely the same integral as α_e (see (6.75)), with the only difference being that the lower limit is now velocity v*, corresponding to threshold of excitation $m_e v^{*2}/2 = E^*$. The dependence of cross section σ_e^* (v) on velocity or on energy (so-called function of excitation) has the same character as the curve of ionization depicted in Fig. 6.4. Exactly so, near the threshold it may be approximated the straight line: $\sigma_e^*(v) = C^*(\varepsilon - E^*)$.* Therefore

$$\alpha_e^* = \int_{v^*}^{\infty} \sigma_e^*(v) v f_e(v) dv = \sigma_e^* \bar{v}_e \left(\frac{E^*}{kT_e} + 2\right) e^{-\frac{E^*}{kT}}, \tag{6.79}$$

where σ_e^* corresponds to energy of electrons E* + kT.

By the principle of detailed balancing, taking into account that

$$\frac{(N^*)}{(N_a)} = \left(\frac{g^*}{g_a}\right) e^{-\frac{E^*}{kT_e}} \tag{6.80}$$

(g^* and g_a are statistical weights of excited and ground state), it is possible to connect constant of speeds α_e^*, β_e^* or effective cross sections of excitation and deactivation:

$$\sigma_{e2} = \sigma_e^* \frac{g_a}{g^*} \left(\frac{E^*}{kT_e} + 2\right); \beta_e^* = \bar{v}_e \sigma_{e2}. \tag{6.81}$$

The characteristic time corresponding to excitation by electron impact, which coincides in time of relaxation for establishment of Boltzmann distribution (6.80) under the condition that T_e = const

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*This is possible for many, but not all atoms; in any case approximation gives small error.

(see footnote on p. 506 is

$$\tau_e^* = \frac{1}{\beta_e^* N_e} = \frac{1}{\bar{v}_e \sigma_{a} N_e}. \qquad (6.82)$$

Source material on cross sections of excitation are in [45, 46]. Certain results are presented in Table 6.5. Mean cross sections of excitation σ_e^* have an order of 10^{-17} cm^2. Such is the order of cross sections of impacts of second kind σ_{e2} (the factor in parentheses in formula (6.81) is of the order of 10, but the ratio of statistical weights g_a/g^* is usually ~1-10^{-1}).

Table 6.5. Excitation by Electron Impact

Atom	Levels	Potential E^*, ev	Interpolation of total cross section σ_e^*, cm^2	Source*
He	$2p^3P$ $2s^1S$	19.7 20.6	$4.6\cdot10^{-18}(\varepsilon_{ev}-20)$ см^2	[46]
Ne	$3s^3P_2$	16.6 18.5	$1.5\cdot10^{-18}(\varepsilon_{ev}-16)$ см^2	[46]
Ar	$4s^3P_2$	11.5	$7\cdot10^{-18}(\varepsilon_{ev}-11,5)$ см^2	[50]
Hg	$6p^3P_1$	4.87	Max. section when $\varepsilon = 6,5$ ev $\sigma_{\max}^* = 1,7\cdot10^{-16}$ см^2	[46]

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*Data with reference [46] are taken from tables given in book of V. L. Granovskiy. References to original works can be found in this book.

For an example we will estimate relaxation time in argon when $T_e = 13{,}000^\circ$K, $N_a = 1.71\cdot10^{13}$ cm^{-3}. Cross sections $\sigma_e^* = 10^{-17}$ cm^2, $\sigma_{e2} \sim 10^{-17}$ cm^2. If one takes equilibrium concentration of electrons $(N_e) = 2.4\cdot10^{17}$ cm^{-3}, we will obtain $\tau_e^* \approx 6\cdot10^{-9}$ sec. This time is considerably less than the time of ionization τ_e. It is interesting to compare characteristic times for ionization and excitation by electron impact. By the formulas (6.73), (6.82)

$$\frac{\tau_e}{\tau_e^{*}}=\frac{\bar{v}_e\sigma_{e2}N_e e^{\frac{I}{kT}}}{\bar{v}_e\sigma_e\left(\frac{I}{kT}+2\right)N_a}\approx\frac{1}{10}\frac{N_e}{N_a}e^{\frac{I}{kT}}\ \text{when}\ \frac{I}{kT}\sim 10.$$

Under conditions close to equilibrium and with small degrees of ionization $N_e/N_a \approx (6\cdot 10^{21}/N_a)^{1/2} T^{3/4}_{ev} \exp(-I/2kT_e)$; for regular densities of gas Boltzmann distribution with respect to excitations is always established faster than ionization equilibrium. In the considered example with argon when $N_a = 1.7\cdot 10^{18}$ cm^{-3}, $T_e = 13{,}000^{\circ}$K, $\tau_e/\tau_e^{*} \approx 5000$. Times can appear comparable only in the beginning of ionization, when the number of electrons is much less than equilibrium.

Unfortunately, there are no data in literature about cross sections of ionization of excited atoms, so that it is fairly difficult to estimate the role of this effect in establishment of ionization equilibrium. Furthermore, here appears the question about the number of practically existing states of atoms in ionized gas (see § 6 Ch. III). Apparently, the cross sections decrease with growth of excitation levels, see § 5 Ch. V, and also § 14 of this chapter). In not too rarefied a gas the upper levels of atoms "are cut," so that the number of actual states is small. It is possible to trust that the above estimates of characteristic times give a true order of magnitude, although rates of ionization, apparently, are understated because ionization of excited atoms is not considered.

The preceding results are easily generalized in the case of a mixture of gases, and also on secondary, etc. ionization.

There is also no data about cross sections of ionization of ions. We must assume that cross sections increase with growth of charge of ions.

§ 13. Ionization and Excitation by Impacts of Heavy Particles

A formal description of these processes is fully analogous to that considered in the preceding sections to the case of ionization and excitation by electron impact. Thus, the equation of kinetics of ionization has the form

$$\frac{dN_e}{dt}=\alpha_a N_a^2-\beta_a N_+ N_e N_a \qquad (6.83)$$

where by the principle of detailed balancing $\beta_\varepsilon = \alpha_a/K(T)$. Characteristic time

$$\tau_a=\frac{(N_e)}{2\alpha_a N_a^2}=\frac{1}{2\beta_a N_a (N_e)}. \qquad (6.84)$$

Constant of ionization rate α_a is expressed by the same formula as α_e. It is necessary only to consider that the effective cross section of ionization $\sigma_a(v')$ depends on relative speed of colliding atoms and as a function of Maxwellian distribution with respect to relative speeds enters reduced mass μ, equal in the case of identical atoms to $\mu = m_a/2$. If, as before, we approximate the cross section near the threshold by linear dependence on kinetic energy of relative motion $\varepsilon' = \mu v'^2/2$, we will obtain for α_a a formula analogous to (6.75). If, however, we simply remove from the integral sign certain mean value of cross section σ_a, instead of factor $I/kT + 2$ the magnitude $I/kT + 1$ will appear close to it. Thus,

$$\alpha_a=\sigma_a\bar{v}'\left(\frac{I}{kT}+2\right)e^{-\frac{I}{kT}}, \qquad \bar{v}'=\left(\frac{8kT}{\pi\mu}\right)^{\frac{1}{2}}, \qquad (6.85)$$

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*Coefficient of recombination equals by definition, $b_a = \beta_a N_a$.

where σ_a corresponds to energy $\varepsilon' \approx I + kT$. It is possible to describe similarly kinetics of excitation.

Unfortunately, in distinction from the case of electron impact, it is very difficult to make any quantitative estimates of rates of the processes. Comparison of constants of rates of ionization by electrons and atoms by the formulas (6.85), (6.75) shows that $\alpha_e/\alpha_a = (\bar{v}_e/v'_a)(\sigma_e/\sigma_a)$. At comparable temperatures $\bar{v}_e/\bar{v}'_a \approx$ $\approx \sqrt{m_a/m_e} \sim 100$. Regarding, however, cross sections, then the only thing that it is possible to say is that σ_e is several orders larger than σ_a. There are no experimental data about cross sections of ionization or excitation by atoms with energies of the order of ten ev, since cross sections are so small that they cannot be measured.

So that a collision is nonelastic, it is necessary that the impact be sufficiently sharp; in other words, the rate of rapprochement of particles should be of the order of speeds of orbital electrons in an atom. In the case of an electron impact with energy of the order of ionization potential or excitation energy, i.e., the order of several or ten ev, this condition is fulfilled and the nonelastic cross section is great. Upon collisions of heavy particles speeds are comparable only when energies are approximately $\sqrt{m_a/m_e} \sim 100$ times larger than the shown magnitudes, i.e., at energies of the order of a kilo-electron-volt. And indeed, here the effective cross section of ionization or excitation is comparable with analogous cross sections for electron impact. For energies of the order of 10 ev rate of rapprochement of particles is very small and impact is "adiabatic." The position is fully analogous to the case of excitation of vibrations in molecules, considered in § 4. Exactly so, in order that during a collision a nonelastic energy transfer happens with considerable probability, it is necessary that adiabatic factor $a\nu/v$ be not too great, of the order of unity. Here by ν one should now understand not frequency of vibrations of molecules, but frequency of rotation of an electron along its own orbit ($a\nu$ of the order of velocity of an electron in an atom, since a is of the order of dimensions of an atom). The lowest energies of relative motion* ε', at which ionization was measured by experiment were of the order of 30-40 ev. It was found that the cross section of ionization of argon by atoms and ions of argon when $\varepsilon' = 35$ ev $\sigma_a \sim 3 \cdot 10^{-18}$ cm^2 [51]; for helium by atoms of helium $\sigma_a \sim 2 \cdot 10^{-19}$ cm^2 when $\varepsilon' = 35$ ev [52]; for argon by ions of potassium $\sigma_a \sim 2 \cdot 10^{-19}$ cm^2 when $\varepsilon' \sim 45$ ev.**

As the quantum-mechanical analog of the condition of being adiabatic $a\nu/v \gg 1$ serves the condition $a\nu/v \rightarrow ah\nu/hv = a\Delta E/hv \gg 1$, where ΔE is the nonelastic transformation of energy during collision. The origin of this condition is such. The probability of the process is determined by matrix element of interaction, in which there is the product of wave functions of initial and final states of particles.

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*By experiment usually a beam of fast particles penetrates the gas from "motionless" atoms. Here the threshold of ionization according to energy of incident particles is twice as high as ionization potential. This corresponds to the fact that the reduced mass is twice less than the atomic mass and at a given relative speed $\varepsilon' = \varepsilon/2$; $\varepsilon_{\text{пг}} = 2\varepsilon'_{\text{пг}} = 2I$. [Editors note: Definition for subscript пг is not available.

**In [54] the effective cross sections of nonelastic Ar-Ar and He-He collisions are theoretically calculated and a comparison is made with experimental data [51, 52]. Data on cross sections of ionization during collisions of ions and atoms with energies of the order of several hundreds of ev and higher are in survey [75].

Wave functions of translational motion are described by plane waves $e^{ipr/\hbar}$;* the product of plane waves of initial and final states yields in the integrand an expression of matrix element oscillatory factor $e^{i\Delta pr/\hbar}$, where Δp is change of momentum of incident particle during collision. The integral has a noticeable magnitude, if this factor does not oscillate in a region where there is great energy interaction, i.e., at a distance r of the order of atomic dimensions a. Thus, the condition of great probability of the process is $\Delta p \cdot a/\hbar \lesssim 1$. Change of momentum Δp is of the order $\Delta E/v$, where ΔE is change of kinetic energy of particles, i.e., nonelastic energy transfer. Hence is obtained the condition of considerable probability $a\Delta E/\hbar v \lesssim 1$; the condition of small probability is $a\Delta E/\hbar v \gg 1$.

From this condition, in particular, it follows that there must be great cross sections of processes in which nonelastic transformation of energy ΔE is very small (the so-called case of resonance). And actually, cross sections of ionization of atoms by excited atoms or molecules are great when, on breaking away of electron is expended not kinetic energy of translational motion, but energy of internal degrees of freedom. Thus, a cross section of processes of the type

$$A + B^* \rightarrow A^* + e + B,$$

where excitation energy E^* of particle B is close to ionization potential of particle A, in an order of magnitude close to gas kinetic. Therefore, the process of ionization by heavy particles, especially molecules, is most likely two stage or multistage: first

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*$\hbar = h/2\pi$.

occurs excitation of one of the particles, and then ionization by impact of excited particle (so-called ionization by impact of second kind) or, conversely, breaking away of electron from excited particle. Certain data about these processes can be found in books [45, 46].

The question about estimating rates of ionization and excitation by heavy particles can appear only in examining the most early stage of ionization of "instantly" heated gas, while concentration of electrons is very small, less than 10^{-4}–10^{-5}, i.e., as yet an electron avalanche is not formed.

In order to estimate the lower limit of the time necessary for formation of "initiating" electrons and appearance of electron avalanche, we will consider the following imaginary process. Let us assume that gas is "instantly" heated to high temperature T and liberated electrons instantly obtain the same temperature T as the atoms. In the beginning of the process, while ionization is considerably less than equilibrium, recombination can be disregarded. At first $dN_e/dt = \alpha_a N_a^2$ and $\alpha_a N_a^2 t$. The number of electrons grows linearly in time until the rate of ionization by electron impact is equal to rate of ionization by impacts of atoms and avalanche does not appear. This moment t_1 is determined from the condition $\alpha_e N_a N_e = \alpha_a N_a^2$. Substituting here $N_e = \alpha_a N_a^2 t_1$ and noticing that by formula (6.73) $\alpha_e N_a = \tau_e$, we will obtain $t_1 = \tau_e$. In other words, the minimum necessary time t_1 is equal to characteristic time of development of avalanche.

The real time of "induction" for development of an avalanche can be quite large. It is determined not by the appearance of a sufficient quantity of free electrons, but by heating of electron gas to a temperature high enough to produce noticeable ionization. This time is limited by deceleration of exchange by energy between atoms (ions) and electrons, which lose much energy to nonelastic collisions: ionization and excitation. For the exchange of energy between ions and electrons, see § 16.

The conditions in which atoms are "instantly" heated to a high temperature, after which ionization starts, are fulfilled in a shock wave. The kinetics of ionization in the front of a shock wave and establishment of ionization equilibrium after the front will be the subject of §§ 10, 11 of Ch. VII.

§ 14. Ionization and Excitation by Light Quanta

Photo-ionization and photo-recombination were already considered in Ch. V during calculation of coefficients of absorption and radiation of light; therefore, inevitably it will be necessary for us to repeat here certain reasonings and conclusions of this chapter.

Let us assume for simplicity that all atoms remain in the ground state and during recombination electrons are captured on the ground level. If N_a is the number of atoms in 1 cm^3, $U_\nu d\nu$ is energy content of radiation in spectral interval from ν to $\nu + d\nu$ in 1 cm^3, and $\sigma_{\nu 1}(\nu)$ is the effective cross section of photo-ionization from ground level of atoms, then the number of events of photo-ionization in 1 cm^3 in 1 sec equals

$$Z^{\nu}_{\text{ион}} = N_a \int_{\nu_1}^{\infty} \frac{U_\nu}{h\nu} d\nu \cdot c \cdot \sigma_{\nu 1}(\nu) = \alpha_\nu N_a,$$

where only quantum $h\nu > h\nu_1 = I$; participate in absorption; $\alpha\nu$ is the constant of photo-ionization rate.

Let us designate by $\sigma_{c1}(v)$ the effective cross section of photo-capture of electrons possessing speed v, on the ground level of an atom. Then the number of events of photo-recombination in 1 cm^3 in 1 sec is

$$Z^{\nu 1}_{\text{рек}} = b_\nu N_+ N_e = N_+ N_e \int_0^\infty f_e(v)\, dv \cdot v \cdot \sigma_{c1}(v) \left[1 + \frac{c^3 U_\nu}{8\pi h \nu^3} \right]. \qquad (6.86)$$

The component $c^3 U_\nu / 8\pi h\nu^3$ in the factor under the sign of integration considers processes of induced recombination, corresponding to forced emission of quanta. Energy of emitted quantum is connected with velocity of an electron by the equation of photoeffect

$$h\nu = \frac{m_e v^2}{2} + I. \qquad (6.87)$$

The integral in (6.86) is the coefficient of photo-recombination b_ν.

By the principle of detailed balancing in conditions of full thermodynamic equilibrium differentials in integral expressions for Z^ν_{rec} and Z^ν_{ion} are equal to each other.

Setting as $f_e(v)$ the function of Maxwellian distribution of electrons, and as U_ν – Planck function, using the Saha equation (6.72) and equation of photoeffect (6.87), we will obtain the connection of effective cross sections of photo-ionization and photo-recombination:

$$\sigma_{c1}(v) = \frac{g_1}{g_+} \frac{h^2\nu^2}{m_e^2 v^2 c^2} \sigma_{\nu 1}(\nu). \qquad (6.88)$$

Cross sections of photo-ionization from n-th excited level of atom and photo-capture on n-th level are likewise connected:

$$\sigma_{cn}(v) = \frac{g_n}{g_+} \frac{h^2\nu^2}{m_e^2 v^2 c^2} \sigma_{\nu n}(\nu). \qquad (6.89)$$

Here g_n is the statistical weight of the n-th state of an atom. Frequency ν and velocity of an electron v also are connected by the equation of photoeffect:

$$h\nu = \frac{m_e v^2}{2} + \varepsilon_n = \frac{m_e v^2}{2} + I - w_n, \tag{6.90}$$

where ε_n is binding energy of an electron the n-th state, and w_n is excitation energy of the n-th level of an atom.

Equation of kinetics of ionization for photo-processes has the form

$$\frac{dN_e}{dt} = Z^{\nu}_{\text{ион}} - Z^{\nu}_{\text{рек}} = a_{\nu} N_a - b_{\nu} N_+ N_e. \tag{6.91}$$

Relaxation time for photo-processes:

$$\tau_{\nu} = \frac{1}{b_{\nu}(N_e)} = \frac{(N_e)}{a_{\nu} N_a}. \tag{6.92}$$

Let us estimate the constant of photo-ionization rate, assuming that the density of radiation is close to equilibrium. In distinction from cross sections of impact ionization, which are equal to zero for the threshold of ionization, the cross section of photo-ionization is different than zero for threshold and in many cases, conversely, is maximum when $h\nu = I = h\nu_1$. Thus, for hydrogen-like atoms $\sigma_{\nu 1} = \sigma^0_{\nu 1}(\nu_1/\nu)^3$, where $\sigma^0_{\nu 1} = 7.9 \cdot 10^{-18}$ cm^2, if the charge of the "nucleus" is equal to unity (see formula (5.34)). If, as usually occurs, $I/kT \gg 1$, ionizing quanta are in the Wien part of the spectrum, where $U_{\nu} \sim \exp(-h\nu/kT)$. Removing from under the integral sign (6.85) average value of cross section, which with great accuracy can be put equal to cross section for threshold of ionization, we will obtain after integration

$$a_\nu = \frac{8\pi}{c^2}\frac{I^2}{h^3}\frac{kT}{h}\sigma^0_{\nu_1} e^{-\frac{I}{kT}} = 3.95\cdot 10^{22} T_{\text{эв}} I^2_{\text{эв}} \sigma^0_{\nu_1} e^{-\frac{I}{kT}}\,\text{sec}^{-1}. \qquad (6.93)$$

The coefficient of recombination b_ν can be found either by the principle of detailed balancing: $b_\nu = a_\nu(N_a)/(N_+)(N_e)$, or directly, calculating integral (6.86). It is necessary to note that when $I \gg kT$ the role of the induced recombinations is very small: the factor in brackets in integral (6.86) approximately equals $1 + e^{-h\nu/kT} \approx 1$, since $h\nu > I \gg kT$. For the coefficient of recombination we obtain (when $I/kT \gg 1$):

$$b_\nu = \overline{v_e\sigma_{c_1}(v)} = v_e\sigma_{c_1}, \qquad (6.94)$$

$$\sigma_{c_1} = \frac{g_1}{2g_+}\frac{I^2}{m_e c^2 kT}\sigma^0_{\nu_1} = \frac{g_1}{g_+}\frac{I^2_{\text{эв}}}{T_{\text{эв}}}\sigma^0_{\nu_1}\cdot 10^{-6}\,\text{см}^2, \qquad (6.95)$$

where σ_{c_1} is mean cross section of photo-capture on ground level (v_e is average thermal velocity of electrons).

Mean cross section of photo-capture is inversely proportional to electron temperature. Effective cross sections of photo-ionization and photo-capture at a temperature, correspondingly, of 1 ev, ($\sigma^0_{\nu_1}$; $\sigma_{c_1} = \sigma^0_{c_1}/T_{ev}$) for certain atoms are presented in Table 6.6. Regarding cross sections of ions, if one were to consider them as hydrogen-like systems, then $\sigma^0_{\nu_1} \sim Z^{-2}$, and $\sigma^0_{c_1} \sim I_Z^2 Z^{-2}$. Usually ionization potentials of ions grow with charge, as $I_Z \sim Z\text{-}Z^{-2}$, whence $\sigma^0_{c_1} \sim Z^0\text{-}Z^2$.

Let us compare recombination rate in three-body collisions with participation of electrons and with emission of quantum. By the formulas (6.77), (6.94), (6.95) we will obtain

$$\frac{Z^e_{\text{рек}}}{Z^\nu_{\text{рек}}} = \frac{b_e}{b_\nu} = \frac{\beta_e N_e}{b_\nu} = \frac{1.7\cdot 10^{-16} N_e}{I_{\text{эв}}\sqrt{T_{\text{эв}}}}\,\frac{C\,\text{см}^3/\text{сек}}{\sigma^0_{\nu_1}\,\text{см}^2} \qquad (6.96)$$

Table 6.6. Effective Cross Sections of Photo-ionization from Ground Levels of Atoms and Photocapture of Electrons on Ground Level

Атом	I, ev	g_1	g_+	$\sigma^0_{\nu_1}\cdot 10^{18}$ см²	Moment of cross section σ_{ν_1} after threshold	$\sigma^0_{c1}\cdot 10^{21}$ см²ev
H	13.54	2	1	7.9	Drops $\sim \nu^{-3}$	2.9
Li	5.37	2	1	3.7		0.21
C'	11.24	9	6	10	Drops by twice when $h\nu = I + 10$ ev	1.9
N	14.6	4	9	7.5	Slowly drops	0.7
O	13.57	9	4	3	Almost constant up to $h\nu \sim I + 15$ ev	1.24
F	17.46	6	9	2	Almost constant up to $h\nu \sim I + 15$ ev	0.41
Na	5.09	2	1	0.31	Drops faster than ν^{-3}	0.016
Ca	6.25	1	2	25	Drops $\sim \nu^{-3}$	0.51

Effective cross section $\sigma^0_{\nu_1}$ and data about movement of cross section after threshold are taken from book [55]. Magnitudes $\sigma^0_{c_1}$ are calculated by the formula (6.95).

independently of whether concentration of electrons is equilibrium or not. As can be seen from Tables 6.4 and 6.6, C and $\sigma^0_{\nu_1}$ are of one order ($\sim 5\cdot 10^{-18}$), ionization potentials of atoms $I \sim 10$ ev, typical for region of first ionization temperature $T \sim 1$ ev $= 11{,}600^\circ$K. From (6.96) it follows that recombination in triple collisions predominates above photo-recombination only when density of electrons $N_e > 10^{17}$ 1/cm³. At smaller densities a basic role is played by photo-recombination.

In states close to the thermodynamic state equilibrium (both with respect to degree of ionization, and also with respect to density of radiation), the number of ionizations is close to number of recombinations, i.e., are in that same ratio. Ratio of relaxation times,

$$\frac{\tau_\nu}{\tau_e} = \frac{Z^e_{\text{ион}}}{Z^\nu_{\text{ион}}} = \frac{Z^e_{\text{рек}}}{Z^\nu_{\text{рек}}} \approx 10^{-17}\,(N_e), \qquad (6.96a)$$

i.e., when $N_e < 10^{17}$ 1/cm³ thermodynamic equilibrium is established mainly owing to photo-processes, and when $(N_e) > 10^{17}$ $1/cm^3$ photo-processes play a secondary role.

In the above example with argon when $T = 13{,}000^\circ K$, $N_a = 1.7\cdot10^{18}$ cm^{-3}, $(N_e) = 0.14$, $N_a = 2.4\cdot10^{17}$ cm^{-3}, $\tau_e = 2.9\cdot10^{-5}$ sec, and $\tau_\nu =$ $= 6.2$, $\tau_e = 1.8\cdot10^{-4}$ sec (here it is assumed that $\sigma^0_{\nu_1} = 7.9\cdot10^{-18}$ cm^2 as for hydrogen-like atoms, and I and C are taken from tables), i.e., photo-processes are less essential. By the formula of Saha, for small degrees of ionization $(N_e) \sim \sqrt{N_a}$, so that $\tau_\nu/\tau_e \sim \sqrt{N_a}$: ratio of time grows in proportion to the root of the density of gas (at constant temperature). In the shown example photo-processes will become basic when $N_a < 4 \times 10^{16}$ cm^{-3} $(T = 13{,}000^\circ K)$.

It is interesting to estimate the role of recombinations with capture of electron on excited levels. The coefficient of recombination in general is equal to (compare with formula (6.94))

$$b_\nu = \sum_n \overline{v\sigma_{c_n}(v)}, \qquad (6.97)$$

where summation is produced over all levels n, and averaging is according to Maxwellian distribution of electrons. $\sigma_{c_n}(v)$ is expressed by formula (6.89). For hydrogen-like atoms $\sigma_{\nu_n} \sim 1/n^5$, $g_n = 2n^2$, so that $\sigma_{c_n} \sim 1/n^3$, where ν and v are connected by formula (6.90), in which $\varepsilon_n = I/n^2$. In general, during summation over n appears a question about number of actual levels in the atom, which should be considered (see § 6 Ch. III); however, in this case the sum over n rapidly converges and summation can be approximately extended to $n = \infty$. Magnitude (6.97) is calculated in book Spittser [56]. The coefficient of recombination there is represented in the form $b_\nu = \text{const}\ \varphi(\beta)$, where const depends only on temperature (and charge of "nucleus" Z), and $\beta = I/kT$, where function $\varphi(\beta)$, including sum over n, is tabulated. If one were to consider only capture on ground level, then when $\beta >> 1$ one should consider $\varphi(\beta) = 1$. According to [56] when $\beta = 5$ $\varphi = 1.69$, when $\beta = 10$ $\varphi = 2.02$, when $\beta = 100$ $\varphi = 3.2$. Thus, under the usual conditions encountered in the region of first ionization, when $\beta = I/kT \sim 10$, capture on all excited levels gives approximately the same contribution in recombination, as capture on ground level.

In virtue of the principle of detailed balancing, under the condition that distribution of atoms with respect to excited states – Boltzmann and radiation equilibrium, the same pertains also to photo-ionization. Thus, during photo-ionization the role of ionization of excited atoms is comparable with the role of ionization of unexcited atoms, so that our estimates of rates of photo-ionization and photo-recombinations are understated approximately one time in two.

Apparently, it is also the same with ionization by electron impact and recombination in three-body collisions.

Let us have a few words apropos of excitation and deactivation of atoms by radiation. The lifetimes of excited atoms with respect to spontaneous emission have an order of $\tau_\nu^* \sim 10^{-8}$ sec. Lifetime with respect to deactivation by electronic impacts of second kind by formula (6.82) at an electron temperature of $T_e \approx 1$ ev $\tau_e^* \sim 1.5 \cdot 10^9/N_e$ sec. Deactivation by electrons predominates over spontaneous luminiscence when $N_e \gtrsim 1.5 \cdot 10^{17}$ 1/cm^3, i.e., with those same conditions at which recombination in three-body collisions predominates over photo-recombination.

Under conditions close to thermodynamic equilibrium, there is a similar relationship of rates of excitation of atoms by electrons and light quanta. Let us note that absorption cross sections of resonance ratiation, able to excite atoms, are very great, resonance radiation is practically always equilibrium (medium is always opaque for resonance quanta), so that time $\tau_{\nu}^{*} \sim 10^{-8}$ sec characterizes relaxation time for establishment of Boltzmann distribution with respect to excited states by means photo-excitement of atoms.

§ 15. Ionization and Recombination in Molecular Gases (in Air)*

At very high temperatures, higher than 10,000-15,000°K, mechanisms of ionization in molecular gases in general do not differ from mechanisms of ionization in monatomic gases. At lower temperatures, below ~ 10,000°K, on the first plan come forward processes which are the reverse of dissociative recombination (6.67). They are profitable by the fact that on ionization is expended, besides, thermal binding energy, liberated as a result of unification of atoms into a molecule. Therefore, activation energy of these processes is comparatively small, and they occur at low temperatures much faster than do processes of ionization of atoms or molecules by impacts of particles.

In particular, the basic and the most important mechanism of ionization in air at temperatures lower than 10,000°K is reaction (6.66), which requires minimum consumptions of energy, in all 2.8 ev. All possible mechanisms of ionization in air at temperatures of the order of 10,000°K and lower are considered in detail in the fundamental investigation of Lin and Teare [73],** in which are given

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*This section, based on the most recent works, was added to the book in proofreading and therefore is extraordinarily compressed.

**See also [72].

many data on cross sections and rates of different processes.

For the most important reaction (6.66) the constant of rate is given in the form

$$k_{\text{иониз}} = 5\cdot 10^{-11} T^{\circ\,-1/2} e^{-32\,500/T^{\circ}} \text{ см}^3/\text{sec}$$

The equilibrium constant of this reaction in the interval of temperatures from 300 to 30,000°K is approximated by the formula

$$K = (1.4\cdot 10^{-8} T + 1.2\cdot 10^{-12} T^2 + 1.4\cdot 10^{-16} T^3)\, e^{-\frac{32500}{T}}$$

(T is in °K). The constant of the rate of the reverse reaction – dissociative recombination – according to the principle of detailed balancing is equal to $b_{\text{dis. rec.}} = k_{\text{ion}}/K$ cm^3/sec. For low temperatures this gives $b_{\text{dis. rec.}} NO^+ \approx 3\cdot 10^{-3} T^{\circ\,-3/2}$ cm^3/sec.

The processes of dissociative recombination (6.67) play the most important role in E- and F-layers of the ionosphere (at altitudes greater than 100 km above sea level). A detailed summary of experimental data on coefficients of dissociative recombination $b_{\text{dis.rec.}}$ is in the survey of G. S. Ivanov-Kholodnyy [71]. $b_{\text{dis.rec.}}$ decreases with increase of temperature approximately as $1/T^{1/2}$-$1/T^{3/2}$ (according to various data). For N_2^+ ions when T = 300°K $b_{\text{dis.rec.}} N_2^+ \approx$ $\approx 10^{-6}$ cm^3/sec which corresponds to a very large effective cross section $\sigma \approx 10^{-13}$ cm^3. For O_2^+ and NO^+ ions $b_{\text{dis.rec.}}$ is somewhat less.

Recombination in cold air during comparatively large densities (in D-shell of ionosphere below ~80 km) occurs basically through formation of negative ions of oxygen. Electrons adhere to molecules of oxygen chiefly in triple collisions $O_2 + e + M \rightarrow O_2^- + M$, and then O_2^- ions recombine with N_2^+ or O_2^- ions in paired or triple collisions. The latest data on recombination in cold air, and also on many other nonelastic processes occurring in the ionosphere, are in the survey of Dal'garno [74].

3. Plasma

§ 16. Relaxation in Plasma

In atomic or molecular gas relaxation time for establishment of Maxwellian distribution according to rates is characterized by the time between collisions of particles, i.e., gas kinetic cross sections, which have an order of 10^{-15} cm^2. Gas kinetic cross sections equal approximately $\sigma \approx \pi a^2$, where radius a is of the order of the range of action of interatomic and intermolecular forces of interaction, i.e., of the order of dimensions of particles. There is another character to the forces effective between charged particles of plasma: electrons, ions. Coulomb forces drop with distance very slowly, as $1/r$, and do not have characteristic scale of length. Therefore, the question about "collisions" between charged particles and the question about corresponding relaxation times should be especially considered.

Plasma can be imagined as a mixture of two gases, electron and ionic, with sharply different masses of particles m_e and m. Owing to a sharp distinction of masses between electrons and ions exchange of energy is hampered, since during "collisions" an electron and ion exchange energy which composes only a fraction of the order $m_e/m \ll 1$ of their kinetic energy. Thus, average kinetic energies of electrons and ions, i.e., electron and ionic temperature, can during a comparatively prolonged time strongly differ from each other. Two factors are noted: long-range character of Coulomb forces and sharp distinction of masses of electrons and ions, determine specific peculiarities of plasma.

Let us consider at first the interaction of charged particles with masses of one order. During collisions they can exchange energy comparable with initial energies of particles; therefore, establishment of Maxwellian distribution according to rates, i.e., temperature, requires only several collisions. If by "collision" we understand such interaction of particles at which occurs considerable change of speed and energy, i.e., deflection at a considerable angle (order of 90°), then in the case of charged particles "collisions" occur during their approach on such a distance at which kinetic and potential (Coulomb) energy turn out to be comparable. This characteristic distance r_0 is determined, obviously, from the condition $Z^2e^2/r_0 \approx kT$, where Z is the charge of the particles. Thus, a measure of the effective cross section of "collisions" can be the magnitude

$$\sigma \approx \pi r_0^2 \approx \pi \frac{Z^4e^4}{(kT)^2}. \qquad (6.98)$$

In reality the matter is somewhat more complicated, since in change of velocities of particles, with the Coulomb law of interaction a large role is played by "far" collisions, corresponding to large impact distances (Fig. 6.5).

"Far" collision occur more frequently than "close" ones. In the slow, Coulomb law of drop of forces the total effect of "far" collisions is great in spite of the fact that change of speed in every such collision is small.

Let us estimate this effect. During flight of one particle past another at impact distance r, the force acting on it, in order of magnitude equals $F \sim Z^2e^2/r^2$. Time of action of force $t \sim r/v$, where v is velocity of a particles. Change of speed during flight is of the order of $\Delta v \sim Ft/m \sim Z^2e^2/mvr$. Inasmuch as change of speed Δv can be both positive and also negative, it is natural to characterize interaction by the square of change of speed $(\Delta v)^2 \sim Z^4e^4/m^2v^2r^2$.

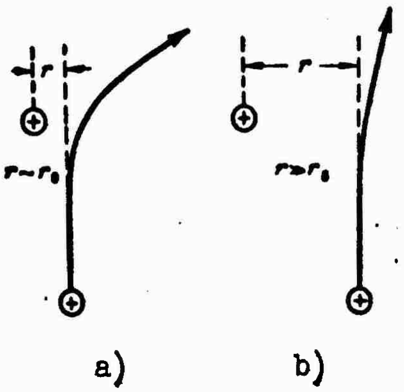

Fig. 6.5. Trajectory of ion during flight past an ion of the same sign: a) r ~ r — strong interaction; b) r >> r — weak interaction.

The probability of such change is proportional to area of ring $2\pi r dr$. Thus, rate of change of magnitude $(\Delta v)^2$ for particle flux Nv is of the order

$$\frac{d(\Delta v)^2}{dt} \sim Nv \int (\Delta v)^2 \cdot 2\pi r dr \sim \frac{NvZ^4e^4 \cdot 2\pi}{m^2v^2} \int \frac{dr}{r},$$

where N is the number of particles in 1 cm^3. The lower limit of the integral is the minimum distance on which particles $r_0 \sim Z^2e^2/mv^2 \sim Z^2e^2/kT$ can approach. On the upper limit, when $r \to \infty$, the integral logarithmically diverges. However, very far interactions in electron-neutral gas are shielded by joint action of positive and negative charges. The radius of shielding, which can be taken as the upper limit, is, obviously, Debye radius d (see § 11 Ch. III). Taking into account formula (3.78) for this magnitude, we will find:

$$\int \frac{dr}{r} \approx \int_{r_0}^{d} \frac{dr}{r} = \ln \frac{d}{r_0} = \ln \Lambda, \quad \Lambda = \frac{3(kT)^{\frac{3}{2}}}{(4\pi)^{\frac{1}{2}} Z^3e^3N^{\frac{1}{2}}}. \tag{6.99}$$

If one determined relaxation time τ as the time during which $(\Delta v)^2$ changes by a magnitude of the order v^2, and put $\overline{mv^2} \sim kT$, we will obtain

$$\frac{1}{\tau} \approx \frac{1}{v^2}\frac{d\,(\Delta v)^2}{dt} \approx N\bar{v}\pi\frac{Z^4e^4}{(kT)^2}\ln\Lambda. \qquad (6.100)$$

Using the usual connection of time of relaxation with "gas kinetic" cross section $1/\tau = N\bar{v}\cdot\sigma$ it is possible to introduce the conditional idea of "effective cross section" also for "collisions" of charged particles. It equals:

$$\sigma \approx \pi\frac{Z^4e^4}{(kT)^2}\ln\Lambda, \qquad (6.101)$$

i.e., $\ln\Lambda$ times more than magnitude (6.98), in which "far" collisions are not considered. As follows from Table 6.7,* $\ln\Lambda$ has order 10.

Table 6.7. $\ln\Lambda$ when $Z = 1$

T, °K \ N, см$^{-3}$	10^{12}	10^{15}	10^{18}	10^{21}
10^3	5.97			
10^4	9.43	5.97		
10^5	12.8	9.43	5.97	
10^6	15.9	12.4	8.96	5.97

More strict consideration (see [56]) leads to the appearance in formulas (6.100), (6.101) of a numerical factor of the order of unity, namely:

$$\sigma = 0.69\pi\frac{Z^4e^4}{(kT)^2}\ln\Lambda = \frac{6\cdot 10^{-6}}{T^{\circ 2}}\ln\Lambda\ \text{см}^2. \qquad (6.102)$$

The effective cross section is very weak, logarithmically depends on density, and is inversely proportional to square of temperature. It is comparable with the usual gas kinetic cross sections $\sigma \sim 10^{-15}$ cm^2 at temperature

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*Data of the table are taken from book [56]. They are somewhat definitized as compared to formula (6.99).

$T \sim 250{,}000^\circ K$.*

Effective cross section σ and length of free path $l = 1/N\sigma$ of charged particles do not depend on mass, i.e., for electrons and ions with equal temperatures they are identical (when $Z = 1$). Relaxation time, owing to dependence on rate, is proportional to the root of mass $\tau \sim 1/\bar{v} \sim m^{1/2}$, i.e., for electrons one time in 100 less than for ions (at equal temperatures).

For instance, in electron gas when $T = 20{,}000^\circ K$, $N_e = 10^{18}\ 1/cm^3$, $\sigma \approx 6 \cdot 10^{-14}\ cm^2$ and $\tau = 2 \cdot 10^{-13}$ sec. In gas from nuclei of hydrogen (protons) with the same temperature and density time is 43 times more, $\tau \approx 8.6 \times 10^{-12}$ sec. From these estimates it is clear that temperature in each of the gases is established very rapidly, so that practically the question about relaxation of establishment of translational temperature almost never appears.

Another matter is the establishment of thermodynamic equilibrium between electron and ionic gases, i.e., equating of electron and ionic temperatures. In a number of physical processes there appears a difference in the temperatures of ionic and electron gases, which with a tendency of the system to thermodynamic equilibrium should disappear with passage of time. Thus, for instance, in a shock wave spreading along plasma, in the shock are heated only ions; electrons remain cold and gradual energy transfer from ions to electrons and equating of their temperatures occur after the shock

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*It is necessary to note that at such large temperatures and energies, at which radius r_0 is less than the radius of ions (complicated) and cross section (6.102) is less than the "gas kinetic" cross section, frequency of collisions and path length of "ions" are determined by this latter, but not by "Coulomb" (6.102).

over a comparatively large time (see § 12 Ch. VII). Let us estimate relaxation time for exchange of energy between ions and electrons and equating of their temperatures.

The "effective cross section" (6.102) does not depend on mass of charged particles and characterizes actually the probability of strong deflection of particles from initial direction of their motion during interaction. The effect of exchange of energy is, so to say, a corollary of deflection. With comparable masses of particles, strong deflection is simultaneously connected also with great energy transfer, in consequence of which cross section σ also determined rate of exchange of energy during collision of identical particles. During interaction of particles with sharply distinguished masses (electrons and ions) exchange of energy during collision, according to law of conservation of momentum and energy, cannot exceed the fraction of order m_e/m. Therefore, so that there is considerable energy transfer, it is necessary that particles undergo approximately m/m_e, i.e., very many "collisions."

Repeating the conclusion of "effective cross section" for "collision" of electrons and ions, let us note that by kinetic energy of colliding particles one should understand kinetic energy of their relative motion. If the electron temperature is not far less than ionic, then relative rate always coincides with velocity of an electron. Reduced mass also coincides with mass of electron, so that average energy of relative motion is characterized by electron temperature. Furthermore, in the expression for effective cross section one of the factors Z^2 pertained to one of the particles, and the second pertained to the other. Inasmuch as for an electron $Z = 1$, instead of Z^4 into the cross section will enter the factor Z^2.

Thus, the "effective cross section" of " collisions" of electrons with ions is of the order $\sigma' \approx \pi Z^2 e^4 \ln\Lambda/(kT_e)^2$, time between "collisions" $\tau' \sim 1/N\bar{v}_e\sigma'$, and characteristic time of exchange:

$$\tau_{ea} \sim \frac{m}{m_e}\tau' \sim \frac{m}{m_e}\frac{1}{N\bar{v}_e\sigma'}. \qquad (6.103)$$

More strict consideration [56] leads to the appearance in this formula of a numerical coefficient of the order of unity. After substitution of values of constants the expression for time of exchange obtains the form

$$\tau_{ea} = \frac{252A\cdot T_e^{\circ\frac{3}{2}}}{NZ^2 \ln\Lambda}\ \text{sec} \qquad (6.104)$$

where A is the atomic weight of ions, and N is their number in 1 cm^3. For instance, when $N = 10^{18}$ cm^{-3}, $T_e = 20{,}000^\circ K$, $Z = 1$, $A = 16$ (atoms of oxygen), $\tau_{ea} \approx 2.8\cdot 10^{-9}$ sec. With a small difference of temperatures of electrons and ions rate of change of temperature of one of the gases is naturally presented in form of the usual equation of relaxation of the type (6.2):

$$\frac{dT_e}{dt} = \frac{T - T_e}{\tau_{ea}}. \qquad (6.105)$$

It turns out, however that the equation of kinetics for temperature balance (6.105) is accurate also with a great difference of temperatures. Equation (6.105) in time of exchange (6.104) (differing

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*In the case of interaction of electrons and complex ions with sufficiently high energies the remark made in the footnote on p. 531 holds true.

by only immaterial numerical coefficient of the order of unity) was for the first time derived by L. D. Landau in 1936 [57] by means of strict consideration of the kinetic equation for gas from charged particles, interacting according to Coulomb's law.

Literature

1. D. F. Hornig. J. Phys. Chem., 61, 856 (1957).

2. E. F. Greene, G. R. Cowan, and D. F. Hornig. J. Chem. Phys., 19, 427 (1951).

3. E. F. Greene, G. R. Cowan, and D. F. Hornig. J. Chem. Phys., 21, 617 (1953).

4. L. V. Leskov and F. A. Savin. UFN, 72, 741 (1961).

5. S. A. Losev and A. I. Osipov. UFN, 74, 393 (1951).

6. I. Zartmann. J. Acoust. Soc. Amer., 21, 171 (1949).

7. A. von Itterbeek and R. Vermaelen. Physica 9, 345 (1943).

8. A. J. Zmuda. J. Acoust. Soc. Amer., 23, 472 (1951).

9. J. V. Connor. J. Acoust. Soc. Amer., 30, 298 (1958).

10. S. Petralia. Nuovo Cimento 10, 817 (1953).

11. J. C. Hubbard. J. Acoust. Soc. Amer., 14, 474 (1952).

12. L. Landau and Ye. Lifshits. Quantum mechanics, I, State Technical Press, 1948.

13. R. Schwartz, Z. Slawsky, and K. Herzfeld. J. Chem. Phys., 20, 1591 (1952).

14. A. I. Osipov. DAN SSSR, 130, 523 (1960).

15. L. Landau, and Ye. Teller. Phys. Z. d. Sowjetunion 10, 34 (1936).

16. V. H. Blackman. J. Fluid Mech., 1, 61 (1956).

17. Zener. Phys. Rev., 37, 556 (1931); 38, 277 (1931).

18. R. Schwartz and K. Herzfeld. J. Chem. Phys., 22, 767 (1954).

18a. K. Herzfeld. Proc. 3 Internat. Congr. Acoust. Stuttgart, v. I, 503, 1959.

19. H. Knötzel and L. Knötzel. Ann. d. Phys., 2, 393 (1948).

20. A. Kantrowitz and A. W. Huber. J. Chem. Phys., 15, 275 (1947).

21. J. T. Herron, J. L. Franklin, P. Bardt, and V. H. Bibeler. J. Chem. Phys., 29, 230 (1958).

22. P. Narteck, R. R. Reeves, and G. Manella. J. Chem. Phys., 29, 608 (1958); 32, 632 (1960).

23. T. Wentink, J. O. Sullivan, and K. L. Wray. J. Chem. Phys., 29, 231 (1958).

24. E. P. Wigner. J. Chem. Phys., 5, 720 (1937); 7, 646 (1939).

25. D. Britton, N. Davidson, W. Gehman, and G. Schott. J. Chem. Phys., 25, 804 (1956).

26. D. L. Bunker and N. Davidson. J. Amer. Chem. Soc., 80, 5085 (1958).

27. R. Fowler and E. Guggenheim. Statistical thermodynamics, IL, 1949.

28. Ye. V. Stupochenko and A. I. Osipov. Journal of Physical Chemistry, 32, 1673 (1958).

29. Ye. V. Stupochenko and A. I. Osipov. Journal of Physical Chemistry, 33, 1526 (1959).

30. O. Matthews. Phys. Fluids 2, 170 (1959). Translation: Problems of Rocket Technology, No. 11, 65 (1959).

31. S. R. Byron. J. Chem. Phys., 30, No. 6, 1380 (1959).

32. N. A. Generalov and S. A. Losev. PMTF, No. 2, 64 (1960).

33. W. G. Zinman. ARS J. 30, 233 (1960). Translation: Problems of Rocket Technology, No. 12, 55 (1960).

34. H. S. Glick and W. H. Wurster. J. Chem. Phys., 27, 1224 (1957).

35. H. B. Palmer and D. F. Hornig. J. Chem. Phys., 26, 98 (1957).

36. D. Britton and N. Davidson. J. Chem. Phys., 25, 810 (1956).

37. Ye. Ye. Nikitin. DAN SSSR, 119, 526 (1958).

38. S. Gleston, K. Ledler, and G. Ehring. Theory of absolute velocities of reactions, IL, 1948.

39. Ya. B. Zel'dovich, P. Ya. Sadovnikov, and D. A. Frank-Kamenetskiy. Oxidation of nitrogen during burning, Publishing House of Academy of Sciences of USSR, 1947.

40. H. S. Click, J. J. Klein, and W. Squire. J. Chem. Phys., 27, 850 (1957).

41. Yu. P. Rayzer. Journal of Physical Chemistry, 33, 700 (1959).

42. D. Kay and L. Libby. Handbook of the experimental physicist, IL, 1949.

43. H. Zeise. Z. Electrochem. 42, 785 (1936).

44. M. Bodenstein. Ramstetter, Z. Phys. Chem., 100, 106 (1922); M. Bodenstein Linder, Z. Phys. Chem., 100, 82 (1922).

45. G. Massey and Ye. Barkhov. Electron and ion collisions, IL, 1958.

46. V. L. Granovskiy. Electrical current in a gas, Vol I, State Technical Press, 1952.

47. M. J. Seaton. Phys. Rev., 113, 814 (1959).

48. W. L. Fite and R. T . Brackmann. Phys. Rev., 113, 815 (1959).

49. Tate and Smith. Phys. Rev., 39, 270 (1932).

50. H. Petschek and S. Byron. Annals of Physics 1, 270 (1957). Translation: Collection, Optical pyrometry of plasma, IL, 1960.

51. A. Rostagni. Nuovo Cimento 13, 389 (1936); Wayland, Phys. Rev., 52, 31 (1937).

52. A. Rostagni. Nuovo Cimento 11, 621 (1934).

53. K. Wray, J. D. Teare, P. Hammerling, and B. Kivel. 8th Sympos. Inter. nat. Combustion, Pasadena, 1960, 84.

54. P. Rosen. Phys. Rev., 109, 348, 351 (1958).

55. V. A. Ambartsumyan, E. R. Mustel', A. B. Severnyy, and V. V. Sobolev. Theoretical astrophysics, State Technical Press, 1952.

56. L. Spitzer. Physics of a completely ionized gas, IL, 1957.

57. L. D. Landau. ZhETF, 7, 203 (1937).

58. N. A. Generalov. Herald of Moscow State University, Physical astronomy, No. 2, 51 (1962).

59. M. Camac. J. Chem. Phys., 34, 448 (1961).

60. W. Poth. J. Chem. Phys., 34, 991 (1961).

61. D. L. Matthews. J. Chem. Phys., 34, 639 (1961).

62. N. H. Johannesen, H. K. Zienkiewicz, P. A. Blythe, and J. H. Gerrard. J. Fluid Mech., 13, 213 (1962).

63. L. R. Hurle and A. G. Gaydon. Nature, N 4702, 184 (1959).

64. W. C. Griffith. Fundam., date obtained shock-tube experim. Oxf., Lond., N. Y., Paris Pergamon Press 242, 1961.

65. L. M. Valley and S. Legvold. Phys. Fluids 3, 831 (1960). Translation: Problems of Rocket Technology, No. 3, 28 (1961).

66. A. I. Osipov. Herald of Moscow State University, Physical astronomy, No. 4, 96 (1960).

67. M. Camac. J. Chem. Phys., 34, 460 (1961).

68. J. P. Rink, H. T. Knight, and R. E. Duff. J. Chem. Phys., 34, 1942 (1961). Translations: Problems of Rocket Technology, No. 4, 58 (1962). Translation/shift: Questions is rocket. Tech., No. 4, 58 (1962).

69. R. W. Patch. J. Chem. Phys., 36, 1919 (1962).

70. R. A. Allen, J. C. Keck, and J. C. Camm. Phys., Fluids 5, 284 (1962).

71. G. S. Ivanov-Kholodnyy. Geomagnetism and aeronomy, 2, 377 (1962).

72. S. C. Lin, R. A. Neal, and W. I. Fyfe. Phys., Fluids 5, 1633 (1962).

73. S. C. Lin and J. D. Teare. Phys., Fluids 6, 355 (1963).

74. A. Dal'garno. UFN 74, No. I, 115 (1963).

75. N. F. Fedorenko. UFN, 668, No. 3, 481 (1959); ZhETF, 38, No. 3 (1960).

76. A. I. Osipov and Ye. V. Stupochenko. UFN, 74, No. I, 81 (1963).

CHAPTER VII

STRUCTURE OF FRONT OF SHOCK WAVES IN GASES

§ 1. Introduction

Basic presentation about shock waves were given in Chapter I. It is shown that equations of hydrodynamics of an idea liquid allow the existence of discontinuous solutions, which describe shock waves. Hydrodynamic magnitudes: density, pressure, speed on both sides of the surface of discontinuity, are interconnected by differential equations corresponding to differential equations which describe regions of continuous flow. These equations are expressions of general laws of conservation of mass, momentum, and energy. From the laws of preservation it follows that on a surface of discontinuity entropy of matter experiences a jump (increases). Magnitude of growth of entropy in a shock wave is determined only by conditions of conservation of mass, momentum, and energy and by thermodynamic properties of matter and absolutely does not depend on the mechanism of dissipation leading to growth of entropy.

In a certain meaning it is paradoxical that equations of adiabatic motion of matter allow the existence of such surfaces on which entropy experiences a jump. The irreversibility of shock compression indicates that in it participate dissipative processes: viscosity and thermal conduction, which leads to growth of entropy.

Namely thanks to viscosity there is carried out an irreversible transformation into heat of a considerable part of the kinetic energy of the gas-dynamic flow incident on the discontinuity in the system of coordinates where the discontinuity rests.

Thus, if one were interested in the mechanism of shock compression, the internal structure and the thickness of that transition layer in which occurs transformation of substance from initial state into final state and which within the bounds of hydrodynamics of an ideal liquid is replaced by a mathematical surface, it is necessary to turn to theory, including a description of the dissipative processes. In Chapter I this question was considered in reference to shock waves of weak intensity. In this chapter limitations will not be put on amplitude of shock wave.

Usually in hydrodynamic processes, changes of macroscopic parameters in regions of continuous flow occur very slowly as compared to speeds of relaxation processes, leading to establishment of thermodynamic equilibrium. Each particle of gas at each moment of time is in a state of thermodynamic equilibrium, corresponding to slowly changing macroscopic parameters, as it were, it "follows" change of these parameters. Therefore, in examining shock discontinuities within the bounds of the hydrodynamics of ideal liquid, states of gas along both sides of discontinuities, with full basis, are assumed to be in thermodynamic equilibrium.

In the thin transition layer where occurs transformation of gas from the initial thermodynamic equilibrium to final thermodynamic equilibrium, density, and pressure, etc., change very quickly. Thermodynamic equilibrium in this region, called the front of the shock wave, can be essentially disturbed. Therefore, during the study of the internal structure of the front of the shock wave it is necessary to take into account also the kinetics of relaxation processes, to consider in detail the mechanism of the establishment of the final state of thermodynamic equilibrium of matter, which is attained behind the front of the wave.

Study of the internal structure of the front of shock waves presents interest from many points of view. At first the question about structure attracted attention as a purely theoretical problem, the solution of which helps us to understand the physical mechanism of shock compression, one of the most remarkable phenomena in gas dynamics. Later shock waves were used in laboratories for the purpose of obtaining high temperatures and investigation of various processes which occur in gases during high temperatures: excitation of oscillations in molecules, dissociation of molecules, chemical reactions, ionization, radiation of light (see Chapter IV).

With the help of theoretical consideration of the structure of the front of a shock wave we derive from experiment valuable information about the speeds of these processes.

Finally, study of the structure of fronts of very strong shock waves, in which radiation plays an essential role, sheds light on the question about such an important characteristic as brightness of the surface of the front of the wave and explains certain interesting optical effects observed by experiment and during strong explosions in air (see Chapter IX).

In the basis of mathematical theory on the structure of the front of a shock wave lies the assumption of stationarity of structure. Time of transformation of matter in a shock wave from initial state to final is very small, much less than characteristic times during which noticeably change parameters of gas in the region of continuous flow behind the front of the wave. Exactly so the width of the front is much less than characteristic scales of length, at which noticeably changes the state of gas behind the front, let us say, distance from front of shock wave to piston, "pushing" wave (piston moves with variable speed).

For that small time, during which the shock wave passes a distance of the order of the width of the front, the speed of its propagation, the pressure and other parameters of gas behind the front practically do not change. But the kinetics of the internal processes occurring in front of the shock wave, spreading along gas with assigned initial parameters, depends only on the amplitude of the wave.

Therefore, during a certain comparatively large interval of time each of particles of gas, flowing in the shock discontinuity, passes through the same sequence of states as the preceding. In other words, distribution of different parameters in the front of the shock wave will form, as it were, a frozen picture, which during this time as a whole moves together with the front (Fig. 7.1).

If speed of front is designated D ($D = |D| > 0$), and a coordinate normal to the surface of the front at a given place of surface is designated x, then it is possible to say that all parameters of the state of the gas inside the wave depend on coordinate and time only in combination $x + Dt$. In the system of coordinates connected with the front, process is stationary establishment and does not depend on time. This circumstance (which, one should mention, already was used during conclusion of relationships in the discontinuity) extraordinarily facilitates the problem from the mathematical point of view, since in the system of coordinates, moving together with the wave, all parameters of the state of the gas are functions not of two variables x and t, but only of one coordinate, and processes are described by ordinary differential equations.

In § 23, Chapter I, in examining the width of the front of shock waves of weak intensity, it was shown that width of compression shock has, for its scale, the mean free path of the molecules. With increase in amplitude of wave, width decreases, and when excess of pressure behind the front over initial pressure becomes comparable with the actual initial pressure, the width of the front becomes of an order of the mean free path.

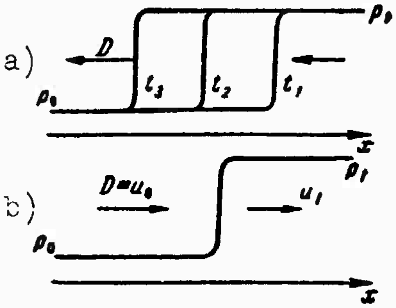

Fig. 7.1. Profile of pressure in a shock wave: a) propagation of shock wave in a laboratory system of coordinates; b) jump in system of coordinates connected with front.

Physically, it is clear that in strong shock waves the width of the shock wave, in which under the action of forces of "viscosity" there occurs shock compression, is always of the order of the mean free path of molecules.* This is simplest of all to explain when one considers shock wave in a system of coordinates in which gas behind the front rests (in a system of coordinates, connected with the piston) or the same when one considers braking of high-speed gas flow incident on motionless wall. The kinetic energy of directed motion

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*It is necessary to emphasize the conventionality of the idea of "viscosity" in this case. When we talk about viscosity, we imply that gradients of speed are small and speeds noticeably change at distances much longer than the length of the mean free path of molecules. In other words, viscosity, which is introduced in hydrodynamics, is a "macroscopic" concept. If a sharp change of speed and density of gas occurs at a distance of the mean free path of molecules, then this phenomenon of "miscroscopic" scale one should consider not hydrodynamically but on the basis of the molecular-kinetic theory of gases. As applied to a case of very large gradients, in front of the shock wave under "viscosity" one should understand the mechanism of transformation of directed velocity of molecules into chaotic velocity, caused by molecular collisions.

of molecules (kinetic energy of hydrodynamic motion) during braking is turned into kinetic energy of chaotic motion, i.e., into heat. For "braking" of fast molecules, the directed speeds of which are much larger than initial thermal speeds (which corresponds to high amplitude of wave: high supersonic speed of wave), several gas kinetic collisions since at each impact a molecule, on the average, changes the direction of its motion to a great angle. Therefore, after several collisions the directional momentum of molecules is almost completely dispersed and speeds become chaotic.

For distribution of energy on different internal degrees of freedom — excitation of oscillations in molecules, dissociation, ionization — there is required usually many collisions. Width of the relaxation layer, in which occurs establishment of final, thermodynamically equilibrium state, is much larger than the width of the initial compression shock. The whole transition layer of the front of the shock wave it is possible, consequently, to divide into two zones, essentially distinguished in their width: a very thin, "viscous" shock wave and an extended relaxation layer.

In a sufficiently strong shock wave, in which gas is heated to high temperatures, an essential role is played by radiation and radiant heat exchange. The structure of the front is still more complicated. Width of front is determined by the biggest scale characterizing the transition process connected with radiant heat exchange: by the length of the mean free path of radiation, which is usually many times larger than the gas kinetic mean free paths of particles.

In subsequent paragraphs there will be considered in detail the peculiarities of structure of the front of shock waves. We will start from consideration of shock waves of comparatively small intensity and will pass to more and more powerful waves.

1. Compression Shock

§ 2. Viscous Shock Wave

Inasmuch as the process of shock compression in the shock wave develops at distance commensurable with gas kinetic molecular path, during the study of the structure of compression shock, one ought, strictly speaking, to start from concepts of molecular-kinetic theory of gases. However, as a first step in this direction it is natural to consider the problem within the bounds of the hydrodynamics of real liquid, taking into account dissipative processes: viscosity and thermal conduction. Besides, in distinction from calculations in § 23, Chapter I, we will not put limitations on amplitude of shock wave. For the purpose of continuity of account we will repeat here certain conclusions and computations from § 23, Chapter I. In order not to complicate consideration by (immaterial in this case) parts connected with retarded excitation of nonprogressive degrees of freedom of gas, we will consider gas monatomic and disregard ionization.

Let us record equations of one-dimensional flow of viscous and heat-conducting gas, stationary in the system of coordinates connected with front of wave:

$$\left.\begin{aligned} &\frac{d}{dx}\varrho u=0, \\ &\varrho u\frac{du}{dx}+\frac{dp}{dx}-\frac{d}{dx}\frac{4}{3}\mu\frac{du}{dx}=0, \\ &\varrho uT\frac{d\Sigma}{dx}=\frac{4}{3}\mu\left(\frac{du}{dx}\right)^2-\frac{dS}{dx}. \end{aligned}\right\} \qquad (7.1)$$

Here Σ is specific entropy; μ is coefficient of viscosity,* S is nonhydrodynamic energy flow equal, in the case of usual thermal conduction, to

$$S=-\varkappa\frac{dT}{dx}, \qquad (7.2)$$

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*In this case, ideas of first and second viscosity are indiscernible.

where $\varkappa$ is coefficient of thermal conduction.

To the system of equations (7.1) one should join boundary conditions, expressing the absence of gradients "before" and "after" front of wave, and the tendency of hydrodynamic magnitudes toward initial (at $x = -\infty$) and final (at $x = +\infty$) values. Converting the third equation of (7.1) with the help of the second law of thermodynamics:

$$T d\Sigma = d\varepsilon + p\,dV = dw - \frac{1}{\varrho} dp$$

and integrating all equations (7.1), we will obtain first integrals of system:

$$\left.\begin{aligned} &\varrho u = \varrho_0 D, \\ &p + \varrho u^2 - \frac{4}{3}\mu\frac{du}{dx} = p_0 + \varrho_0 D^2, \\ &w + \frac{u^2}{2} + \frac{1}{\varrho_0 D}\left(S - \frac{4}{3}\mu u\frac{du}{dx}\right) = w_0 + \frac{D^2}{2}. \end{aligned}\right\} \tag{7.3}$$

Constants of integration here are expressed through parameters of initial state of gas to which is ascribed index "0" and speed of front $D \equiv u_0$.

If one were to carry equations (7.3) to final state (to parameters of it we will ascribe index "1"), we will obtain already known relationships on discontinuity, which for convenience we will write out once again:

$$\left.\begin{aligned} \varrho_1 u_1 &= \varrho_0 D, \\ p_1 + \varrho_1 u_1^2 &= p_0 + \varrho_0 D^2, \\ w_1 + \frac{u_1^2}{2} &= w_0 + \frac{D^2}{2}. \end{aligned}\right\} \tag{7.4}$$

From these relationships it follows that the jump of entropy in shock wave $\Sigma_1 - \Sigma_0 = \Sigma(p_1, \rho_1) - \Sigma(p_0, \rho_0)$ absolutely does not depend on mechanism of dissipation nor on magnitude of coefficients of viscosity and thermal conduction μ and $\varkappa$. The last ones determine only internal structure of front of wave and its thickness δ. Thickness of viscous shock wave δ is proportional to coefficients μ and $\varkappa$, which in turn are proportional to the mean free path of molecules l. In limit $l \to 0$ hydrodynamics of real liquid turn, in regions of continuous flow, into hydrodynamics of ideal liquid. As regards the front of the shock wave, in limit $l \to 0$ it is turned into a mathematical surface, since $\delta \sim l \to 0$. The gradients of all hydrodynamic magnitudes in the front rush to infinity as $1/l$, and jumps of magnitudes remain final.

Assigning as coefficients of viscosity and thermal conduction, and also thermodynamic bond $w(p, \rho)$ (in monatomic gas $w = c_pT = \frac{5}{2}p/\rho$), it is possible numerically to integrate equations (7.3), (7.2) with the shown border conditions. It is much more convenient, however, to deal with analytic solution since it more graphically demonstrates all laws of the phenomenon. Unfortunately, in general, we cannot find analytic solution of the system. To integrate equations analytically it is possible if one were to be limited by waves of weak intensity and to expand the solution in a series with respect to small changes of one of the gas-dynamic magnitudes. This method was used in § 23, Chapter I for appraisal of width of a front (full solution is in a book of L. D. Landau and Ye. M. Lifshits [1]).

Exact analytic solution for a wave of arbitrary amplitude can be found in one special case. This solution, obtained for the first time by Becker [2] and later investigated by Morduchow and Libby [3], describes all the physical regularities of the structure of a compression shock, while possessing simplicity and clarity. Let us pause on it in greater detail.

Usually in gases transport coefficients -- kinematic viscosity $\nu = \mu/\rho$ and temperature transfer $\chi = \varkappa/c_p\rho$ — are close to one another and to coefficient of diffusion $l\bar{v}/3$.

We will assume combination $\Pr = \mu c_p/\varkappa = \nu/\chi$, called Prandtl number, to be equal to 3/4. In this case, the expression in parentheses in the third of the equations (7.3) is turned into a total differential of magnitude $w + \frac{u^2}{2}$ and the equation takes the form

$$\left(w+\frac{u^2}{2}\right)-\frac{4}{3}\frac{\mu}{\varrho_0 D}\frac{d}{dx}\left(w+\frac{u^2}{2}\right)=w_0+\frac{D^2}{2}.$$

after writing an integral of this linear equation, we will see that condition of finiteness of magnitude $w + \frac{u^2}{2}$ at $x = +\infty$ it is possible to satisfy only considering it not depending on x:

$$w+\frac{u^2}{2}=w_0+\frac{D^2}{2}{}^{*)}. \qquad (7.5)$$

Thus, during Prandtl number Pr = 3/4 relationship (7.5) is fulfilled not only after front of wave (see (7.4)) but also at any intermediate point x.

Equation (7.5) gives a curve on plane p, V, along which occurs transformation of gas from initial state to final. Noticing that in monatomic gas, which we will consider here, $w = 5/2\ pV$, and passing to dimensionless speed or specific volume

$$\eta=\frac{u}{D}=\frac{V}{V_0}=\frac{\varrho_0}{\varrho},$$

will find equation of this circle:

$$\frac{p}{p_0}=\frac{1+\frac{M^2}{3}(1-\eta^2)}{\eta}=\frac{4\eta_1-\eta^2}{(4\eta_1-1)\eta}. \qquad (7.6)$$

Here η_1 pertains to final state after front of shock wave:

$$\eta_1=\frac{1}{4}+\frac{5}{4}\frac{p_0}{\varrho_0 D^2}=\frac{1}{4}+\frac{3}{4}\frac{1}{M^2}. \qquad (7.7)$$

M — is Mach number equal to $M = D/c_0$, where c_0 is speed of sound in initial state ($c_0^2 = 5/3\ p_0V_0$). At conclusion of formulas (7.6), (7.7) were used relationships connecting magnitudes along both sides of the front of the wave. The shock adiabat in variables p_1/p_0, η_1 has the form

$$\frac{p_1}{p_0}=\frac{4-\eta_1}{4\eta_1-1}.$$

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*This equation is analogous to Bernoulli integral in the theory of stationary flow.

In Fig. 7.2 are depicted shock adiabat and curve along which changes the state of a particle in the wave (and also the characteristic straight line connecting initial and finalstates).

With the help of formula (7.6) and the first two equations of (7.3) we write a differential equation determining profiles of speed and volume in the front of the wave $\eta(x)$:

$$\frac{5}{3}\frac{\mu}{\varrho_0 D}\eta\frac{d\eta}{dx} = -(1-\eta)(\eta-\eta_1). \qquad (7.8)$$

We will, for simplicity, consider the coefficient of viscosity to be not dependent on temperature and equal to $\mu = \rho_0 l_0 \bar{v}_0/3$ (on density coefficient of viscosity does not depend, since $\mu \sim \rho l$, and $l \sim 1/\rho$). Integral of equation (7.8) contains an additive constant in accordance with the arbitrary nature in the selection of the origin of coordinates. Placing the origin of coordinate at the point of inflection of the profile of speed (in the "center" of the wave) and taking into account formula (7.7), we will find for $\eta(x)$ expression:

$$\frac{1-\eta}{(\eta-\eta_1)^{\eta_1}} = \frac{1-\sqrt{\eta_1}}{(\sqrt{\eta_1}-\eta_1)^{\eta_1}} e^{a\frac{M^2-1}{M}\frac{x}{l_0}} \left(a=\frac{27}{40}\sqrt{\frac{5\pi}{6}}=1,1\right). \qquad (7.9)$$

Knowing profile of speed $u = D\eta$, it is already easy to determine profiles of all other magnitudes. Thus, for temperature, according to formula (7.5) we have $T/T_0 = 1 + \frac{M^2}{3}(1 - \eta^2)$; pressure is determined through formula (7.6); entropy is equal to:

$$\Sigma-\Sigma_0 = c_p'\ln\frac{T}{T_0} - A\ln\frac{p}{p_0} \quad \left(A=\frac{p}{\varrho T}\right).$$

From formula (7.9) one may see that at $x \to -\infty$ $\eta \to 1$, and at $x \to +\infty$, $\eta \to \eta_1$, where approach to initial and final values occurs asymptotically, according to exponential law. All hydrodynamic magnitudes in the wave – speed, density, pressure, and

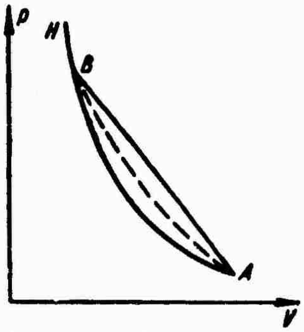

Fig. 7.2. Shock transition A → B on p, V diagram. H is shock adiabat. A point describing the state inside the front of the wave passes from A to B along dotted curve.

temperature — monotonically are changed from their initial to their final values and asymptotically approach them at $x \to \mp\infty$.*

Entropy changes nonmonotonically and inside wave attains maximum (already shown in § 23, Chapter 1). This is easily seen if one converts the third, entropic, equation (7.1) with the help of the second law of thermodynamics, "Bernoulli's integral" (7.5), of the second of the equations (7.1), and conditions of constancy of the coefficient of viscosity are:

$$\varrho u T\frac{d\Sigma}{dx}=\varrho u\left(\frac{dw}{dx}-V\frac{dp}{dx}\right)=\varrho u\left(-u\frac{du}{dx}-V\frac{d}{dx}\frac{4}{3}\mu\frac{du}{dx}+V\varrho u\frac{du}{dx}\right)=$$
$$=-u\frac{d}{dx}\frac{4}{3}\mu\frac{du}{dx}=-\frac{4}{3}\mu u\frac{d^2u}{dx^2}.$$

Hence it is clear that entropy is extreme at the point of the bend in speed, i.e., in the "center" of the wave. Appearance of maximum of entropy in the wave is connected with the existence of thermal conduction. One of the dissipative processes, viscosity, leads only to growth of entropy, proportional to $(du/dx)^2$. Owing to thermal conduction, heat in irreversible form is transferred from the more heated layers of gas to the less heated. The increase in entropy of particles because of thermal conduction in the less heated layers, where $\frac{dS}{dx} \sim -\frac{d^2T}{dx^2} < 0$, is positive, and in the more heated layers, where $dS/dx \sim -\frac{d^2T}{dx^2} > 0$, is negative.

Decrease of entropy in the more heated layers of gas in now way contradicts the second law of thermodynamics. Entropy of all the gas on the whole of of separate particles, as a result of the entire process of shock compression, increases during transition through shock discontinuity. A separate layer of gas passing through the wave no longer constitutes an isolated system. Its entropy in the beginning grows when to it proceeds heat, thanks to thermal conduction and work of the

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*Points where various magnitudes in the front of the wave experience a bend do not coincide.

forces of viscosity, but then decreases when departure of heat, because of thermal conduction in the direction of the layers of gas following after the one considered, exceeds flow owing to the work of the forces of viscosity.

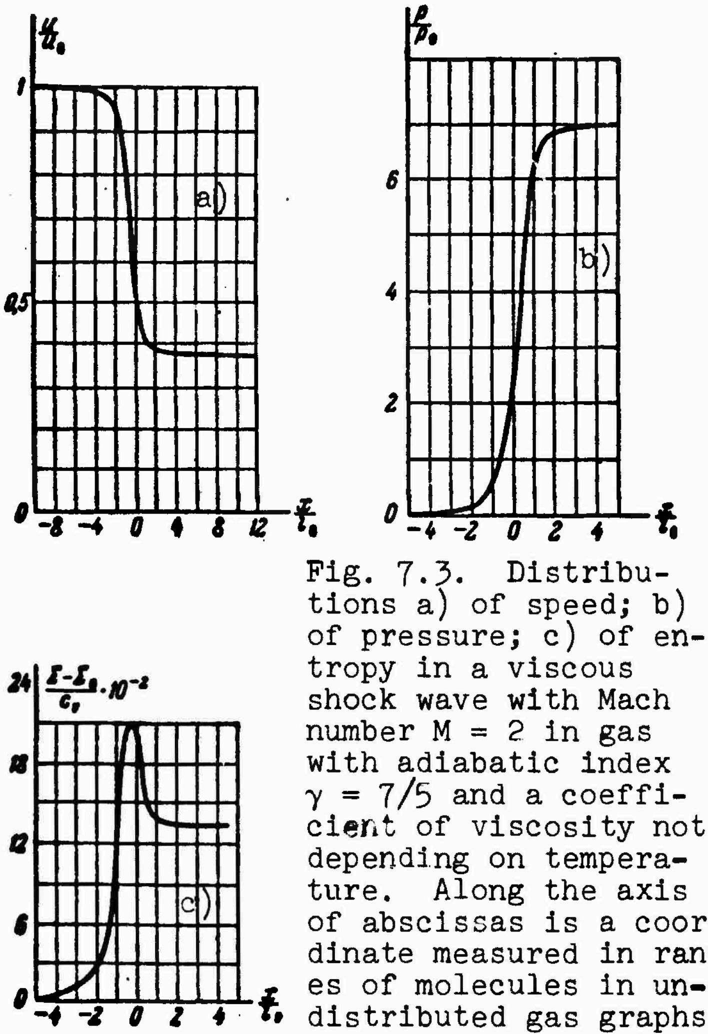

Fig. 7.3. Distributions a) of speed; b) of pressure; c) of entropy in a viscous shock wave with Mach number M = 2 in gas with adiabatic index $\gamma = 7/5$ and a coefficient of viscosity not depending on temperature. Along the axis of abscissas is a coordinate measured in ranges of molecules in undistributed gas graphs are taken from [3]).

Let us define width of front, as also in § 23, Chapter I, by condition

$$\delta = (D - u_1)\Big/\left(\frac{du}{dx}\right)_{\max}.$$

From formula (7.9) it is clear that width of front in order of magnitude is equal to

$$\delta \sim l_0 \frac{M}{M^2 - 1}.$$

In a shock wave of small amplitude, when $M - 1 \ll 1$, $\delta \sim l_0/(M - 1)$

in accordance with results of § 23, Chapter I. Width of wave can equal many mean free paths of molecules. In a limiting case of a strong wave, when M >> 1, formally $\delta \sim l_0/M \rightarrow 0$.

In the case M = 2, depicted in Fig. 7.3, the width of the front is equal to approximately three mean free paths l_0. The trend of the width of the front toward zero with an increase of amplitude of wave should not, of course, be understood literally. The matter is simply that when the width of the front becomes of the order of a mean free path, hydrodynamic theory loses meaning, since in the basis of it lies an assumption of the smallness of gradients, i.e., the smallness of range as compared to distances at which there occur considerable changes of hydrodynamic parameters. Therefore, to sufficiently strong waves the theory is simply not applicable. Physically, it is clear that the thickness of the shock wave in a wave of any amplitude cannot become less than a mean free path since molecules of gas, incident on the discontinuity, must make at least several collisions so that directional momentum disperse and kinetic energy of directed motion be turned into kinetic energy of chaotic motion (into heat). At the same time, the thickness of shock wave in the case of a strong wave cannot compose many paths since in each collision, molecules of incident flow lose, on the average, a considerable fraction of their momentum.

The problem about the structure of strong compression shocks should be considered on the basis of the molecular-kinetic theory of gases; therefore, numerous investigations directed toward a more precise definition of the above-stated simple theory, calculation of the dependence of transport coefficients on temperature, and clarification of the influence of the Prandtl number on the structure of the front, etc., [4-13] do not introduce anything new in principle as compared to the considered particular case, and in the best case present interest for waves of weak intensity.*

I. Ye. Tamm and, independently, Mott-Smith [16] applied a kinetic Boltzmann equation to the problem about structure of a shock wave. Approximate solution of the Boltzmann equation in the region of the jump is constructed in the form of the superposition of two Maxwellian distributions corresponding to temperatures and macroscopic speeds in the initial and final states. The relative weight of both functions changes, during the period of the wave, from 0 to 1. Thickness of the front during unlimited growth of amplitude of shock wave aspires to the final limit. By the calculations of Sakurai [17], which have somewhat improved the method of Mott-Smith, in a model of solid spheres for the interaction of molecules, widths of compression shocks, measured in lengths of free path during initial conditions, are equal** to: $\delta/l_0 = 2.11$; 1.68; 1.46; 1.42 during Mach numbers equal to $M = 2.5$; 4; 10; ∞ respectively.

In recent years there have appeared several works in which there is developed Mott-Smith method and a shock wave is considered on the basis of Boltzmann equation [52-55].

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*Attempt at more precise definition of the hydrodynamic approach by means of calculation of second derivatives in expressions for members of transfer (the so-called approach of Barnett), undertaken by Zoller [14], somewhat definitizes results for weak waves and, essentially, only indicates limits of applicability of hydrodynamic theory. During amplitude of wave $p_1/p_0 = 1.5$ thickness of wave, according to Zoller, is equal to 17 mean free paths, but during $p_1/p_0 = 4$ it is equal to 6 paths. Widths of fronts of weak shock waves in monatomic gases were measured by the method of light reflection in the works of Cowan, Hornig, and others [15] (see § 5, Chapter IV). The width turned out to be equal to 30, 19, and 13 paths for Mach numbers $M = 1.1$; 1.5; 2.5, respectively. Calculations of Zoller give good agreement with these results. See also [56].

**Width of front δ is determined in the following way. If f_α and f_β are distribution functions of molecules in initial and final states, then for a distribution function at intermediate point of wave x theory gives $f = \nu(-x)f_\alpha + \nu(x)f_\beta$, where

$$\nu(x) = \frac{1}{2}\left(1 + \mathrm{th}\,\frac{2x}{\delta}\right).$$

§ 3. The Roles of Viscosity and Thermal Conduction in the Formation of a Shock Wave

In spite of the fact that transport coefficients – kinematic viscosity and temperature conductivity – just as the corresponding dissipative members in the equation of energy, are comparable among themselves, the roles of both the dissipative processes in the formation of a shock wave by far are not equivalent. Physically, it is clear that a fundamental role in the mechanism of shock compression is played by viscosity, but not by thermal conduction, since namely the mechanism of viscosity leads to the scattering of directed momentum of the incident gas flow and transformation of the kinetic energy of directed motion of molecules into kinetic energy of chaotic motion, i.e., transformation of mechanical energy into heat. Thermal conduction only transfers thermal energy from some layers of gas to others and influences transformations of mechanical energy by indirect form thanks to redistribution of pressure.

In order to see this, it is useful to consider the problem about one-dimensional stationary motion of gas with boundary conditions corresponding to shock compression of undisturbed flow on the assumption that viscosities, in general, are lacking, and dissipation is responsible exclusively to thermal conduction. The investigation of this question, for the first time conducted by Rayleigh [18], has a fundamental value, since it reveals peculiarity of structure of the front of a shock wave in the presence of other mechanisms of heat exchange: radiant transfer of energy or electron thermal conduction (in plasma).

If one were to not consider viscosity, then first integrals of equations of hydrodynamics of a one-dimensional stationary flow (7.3) take the form:

$$\left.\begin{aligned} \rho u &= \rho_0 D, \\ p + \rho u^2 &= p_0 + \rho_0 D^2, \\ w + \frac{u^2}{2} + \frac{S}{\rho_0 D} &= w_0 + \frac{D^2}{2}. \end{aligned}\right\} \qquad (7.10)$$

From the first two equations (7.10) it follows that in the process of shock compression, in the absence of viscosity, the state of a particle of gas must continuously change along a straight line on the pressure — specific volume diagram

$$p = p_0 + \rho_0 D^2 (1 - \eta), \quad \eta = \frac{V}{V_0}. \qquad (7.11)$$

This important property of the flow of nonviscous gas is illustrated in Fig. 7.4, on which is depicted shock adiabat and a straight line connecting initial and final states of gas. Let us try to solve a system of equations (7.10), for which, as earlier, we will exclude all variables besides dimensionless speed or relative specific volume η. For generality we will not be limited by the case of monatomic gas and will preserve arbitrary magnitude of adiabatic index γ, which we will consider constant.

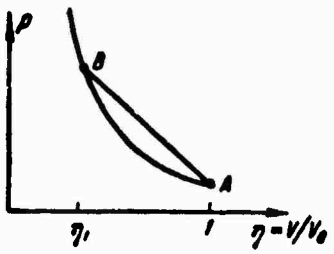

Fig. 7.4. Straight line of impact transmission for a nonviscous gas.

Considering equation of state

$$p = \frac{R}{\mu_0} \rho T = A \rho T, \quad A = \frac{R}{\mu_0} \qquad (7.12)$$

(μ_0 is molecular weight) and thermodynamic bond $w = \frac{\gamma}{\gamma - 1} \frac{p}{\rho}$, we will express from the third equation of (7.10) and equation (7.11) nonhydrodynamic energy flow and temperature through η:

$$\frac{T}{T_0} = 1 + \gamma M^2 (1 - \eta) \left(\eta - \frac{1}{\gamma M^2} \right), \qquad (7.13)$$

$$S = -\frac{\rho_0 D^2}{2} \frac{\gamma + 1}{\gamma - 1} (1 - \eta)(\eta - \eta_1). \qquad (7.14)$$

Here, as earlier, magnitude

$$\eta_1 = \frac{\gamma-1}{\gamma+1} + \frac{2}{\gamma+1}\frac{1}{M^2}$$

is dimensionless speed in final state, and $M = D/c_0$ is Mach number.

Function $T(\eta)$ passes through maximum, finding at point

$$\eta = \eta_{\max} = \frac{1}{2} + \frac{1}{2\gamma M^2}.$$

In examining shock waves of different amplitude there can be presented two cases. If amplitude is sufficiently small, then $\eta_1 > \eta$. Really, at Mach number close to unity ($M - 1 << 1$), $\eta_1 \approx 1 - \frac{4}{\nu+1}(M - 1)$, i.e., also close to unity, whereas $\eta_{\max} \approx (\gamma + 1)/2\gamma < 1$. In this case, during monotonic compression of gas from initial volume to final (from $\eta = 1$ to $\eta = \eta_1$) temperature monotonically increases from initial value T_0 to final T_1, equal (during all conditions) to

$$\frac{T_1}{T_0} = 1 + \frac{2(\gamma-1)}{\gamma(\gamma+1)^2}(M^2-1)\left(1+\frac{1}{\gamma M^2}\right).$$

Graphs of $T(\eta)$ and $S(\eta)$ in this case have the form depicted in Fig. 7.5.

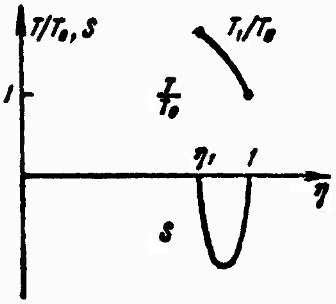

Fig. 7.5. T, η- and S, η-diagram for a case when there is possible continuous shock transition with only thermal conduction without taking into account viscosity.

If one were to exclude η from equations (7.13), (7.14) and to substitute expression (7.2) for flow S, we will obtain differential equation of type $dT/dx = f(T)$, which has continuous solution. Profiles of temperature and entropy in such a wave are schematically depicted in Fig. 7.6; they are similar to profiles found in preceding paragraph.

As can be seen from entropy equation (7.1) $\mu = 0$, entropy is maximum at a point where $\frac{d}{dx}\varkappa\frac{dT}{dx} = 0$ or, in the case $\varkappa = \text{const}$, at the point where temperature in the wave $T(x)$ has a bend: $d^2T/dx^2 = 0$.

Thus, the existence of a weak shock wave is possible with a continuous distribution of hydrodynamic magnitudes in front and in the absence of viscosity when there is only thermal conduction.

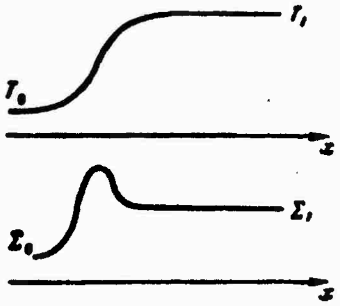

Fig. 7.6. Profiles of temperature and entropy in a shock wave with only thermal conduction, without taking into account viscosity, in a case when continuous transition is possible.

Let us consider now a sufficiently strong shock wave.

In this case the volume at which temperature is maximum is included between initial and finite values: $\eta_1 < \eta_{max} < 1$. Actually, at $M >> 1$ $\eta_{max} \approx 1/2$, and $\eta_1 = (\gamma - 1)/(\gamma + 1) < 1/4$, since the adiabatic index of gas cannot exceed 5/3.

Thus, during monotonic continuous compression of gas from initial volume to final temperature, in the front of the wave it must unavoidably pass through maximum. Graphs of functions $T(\eta)$ and $S(\eta)$ for this case are depicted in Fig. 7.7. Let us see if the existence of continuous solution of equations (7.13), (7.14) in this case is possible. From formula (7.14) and Fig. 7.7 it is clear that flow of heat S, caused by thermal conduction, in the whole interval of change of relative volume from $\eta = 1$ to $\eta = \eta_1$ does not change sign and is directed toward flow of gas: $S < 0$. In accordance with determination of flow $S = -\varkappa dT/dx$, temperature during change of volume from initial to final can only increase: $dT/dx > 0$.

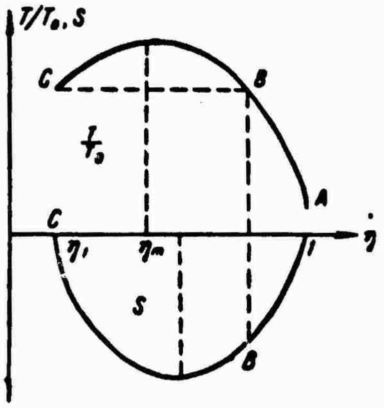

Fig. 7.7. T, η- and S, η-diagram for the case of an isothernal jump during calculation of only thermal conduction, without taking into account viscosity.

Consequently, the region after maximum of temperature, where $dT/d\eta > 0$, is not realized. In this region the volume still does not attain final value and must decrease $d\eta/dx < 0$, temperature drops with decrease of volume, i.e.,

$$dT/dx = (dT/d\eta)(d\eta/dx) < 0,$$

and flow would be directed to the other side ($S > 0$), which contradicts formula (7.14).

Thus, in the case of a strong wave, during calculation of only thermal conduction, continuous distribution of temperature and density on coordinates is impossible. To come from initial state to final, passing region of fall of temperature with increase of compression, is possible only after including in solution discontinuity: namely, state changes continuously from initial (point A in Fig. 7.7.) to point B, and then by jump falls to final point C. Appearance of a jump of density indicates that in it must be manifested forces viscosity, i.e., a strong discontinuity can be blurred only thanks to viscosity, but not thermal conduction. Temperature in the jump remains constant; only its derivative changes, i.e., flow. Profiles of temperature and density in such a wave, called "isothermal" discontinuity are depicted in Fig. 7.8.*

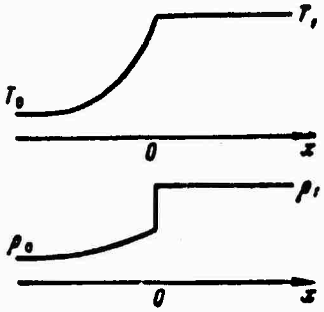

Fig. 7.8. Profiles of temperature and density in a shock wave with isothermal discontinuity.

It is easy to find the biggest amplitude at which continuous solution in the absence of viscosity is still possible. It corresponds to a case when maximum of function $T(\eta)$ coincides with final state, i.e., $\eta_{max} = \eta_1$.

Mach number and pressure ratio along both sides of front are equal to:

$$M' = \sqrt{\frac{3\gamma-1}{\gamma(3-\gamma)}}, \quad \frac{p_1'}{p_0} = \frac{\gamma+1}{3-\gamma};$$

for instance, at $\gamma = 5/3$ $M' = 1.35$, $p_1'/p_0 = 2$; at $\gamma = 7/5$ $M' = 1.2$, $p_1'/p_0 = 1.5$.

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*Let us note that the "isothermic" nature of the jump, i.e., continuity of temperature in the shock wave, is caused by the fact that heat flow is assumed proportional to gradient of temperature. In the third section of this chapter, in examining radiant heat exchange in the front of the shock wave, we will see that if one were to not make such an assumption, then the value of temperature also would have a discontinuity.

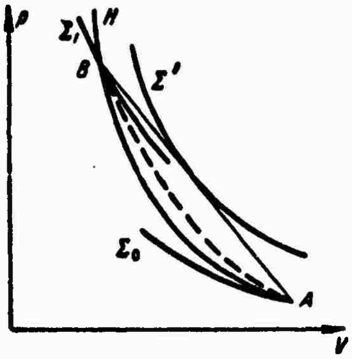

Fig. 7.9. p, V-diagram for shock wave taking into account viscosity. H — shock adiabat; Σ_0, Σ_1, Σ' adiabats of Poisson; along the dotted curve occurs transition from initial state to final.

If we consider the other extreme case, when there is only viscosity and there is no thermal conduction, we will obtain a continuous solution for hydrodynamic magnitudes in the shock wave, in principle not differing from solution of preceding paragraph, with the only exception that entropy in this case increases also monotonically (see third equation of (7.1) without member dS/dx). The course of entropy in both extreme cases it is possible to comprehend by means of the consideration of diagram p, V or p, η (Fig. 7.9). In the absence of viscosity the state in the wave changes along straight line AB, and entropy, as can be seen from comparison of shock adiabat and adiabats of Poisson, in the beginning, grows, attains a maximum at point of contact of straight line with adiabat of Poisson Σ', and then decreases. In the absence of thermal conduction, the state changes along dotted curve, passing below straight line AB (equation of this curve is $p = p_0 + \rho_0 D^2(1 - \eta) + \frac{4}{3} \mu \frac{du}{dx}$, where $du/dx < 0$), and it nowhere touches adiabats of Poisson. The position here is fully analogous to that which takes place in the waves of weak intensity, considered in § 23, Chapter I.

§ 4. Diffusion in a Binary Mixture of Gases

If in a mixture of gases there are gradients of thermodynamic magnitudes, then there appears diffusion flow of components of the mixture, thanks to which there occurs redistribution of their concentrations. In general, diffusion tries to equalize concentration of components in space. However, during the existence of gradients of pressure, temperature, or in the field of external forces: gravity, centrifugal force in a revolving mixture, and, in general, in the presence of accelerations, there occurs separation of an initially uniform mixture.

In particular, such a situation appears in a shock wave spreading along a mixture of gases. Before and after the front of the wave concentrations of components are identical and constant in space. In the region of the front, where there are gradients, concentrations are changed. Like viscosity and thermal conduction, diffusion constitutes an irreversible molecular mass transfer of a defined component (viscosity carries momentum and thermal conduction — internal energy) and is one of the sources of dissipation of mechanical energy.

Diffusion flow is determined in the following way. Let us assume that in a binary mixture of gases mass concentration of one of the components, let us say, the light one with mass of molecules m_1, is equal to α. Concentration of the second, the heavy one, a component with mass of molecules $m_2 (m_2 > m_1)$ is $1 - \alpha$.* Thanks to diffusion of one gas relative to other gases they possess different macroscopic speeds. Let us designate them through $\mathbf{u}_1$ and $\mathbf{u}_2$. If ρ is density of mixture, then total flux of first component is $\rho\alpha\mathbf{u}_1$, and flow of second is $\rho(1 - \alpha)\mathbf{u}_2$. Macroscopic or hydrodynamic speed of mixture $\mathbf{u}$ is determined so that total flux of mass of gas is equal to $\rho\mathbf{u}$ ($\mathbf{u}$ is momentum of a mass unit). Thus, $\rho\mathbf{u} = \rho\alpha\mathbf{u}_1 + \rho(1 - \alpha)\mathbf{u}_2$ or $\mathbf{u} = \alpha\mathbf{u}_1 + (1 - \alpha)\mathbf{u}_2$. Within the bounds of hydrodynamics of an ideal liquid speeds of both components of the mixture coincide and equal $\mathbf{u}$. Flows of components are equal to $\rho\alpha\mathbf{u}$ and $\rho(1 - \alpha)\mathbf{u}$.

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*Mass concentration α is equal to mass of first, light component in one gram of mixture. If the number of molecules in one gram of mixture is N_1 and $N_2 (N_1 + N_2 = N)$, then $\alpha = N_1 m_1$, $1 - \alpha = N_2 m_2$. Molar concentrations are equal to

$$\frac{N_1}{N} = \frac{\alpha}{N m_1}; \quad \frac{N_2}{N} = \frac{1-\alpha}{N m_2}.$$

In the following approach, in hydrodynamic theory there are viscosity, thermal conduction, and diffsuion (in the mixture). Diffusion flow **i** is the difference between full and hydrodynamic flows of one, let us say, the first component, $i = \rho\alpha u_1 - \rho\alpha u = \rho\alpha(u_1 - u)$.

Total flux of first component is equal to the sum of hydrodynamic and diffusion $\rho\alpha u + \mathbf{i}$. Total flux of the second component, obviously, is equal to $\rho(1 - \alpha)u_2 = \rho(1 - \alpha)u + \rho(1 - \alpha)(u_2 - u) = \rho(1 - \alpha)\,u - \mathbf{i}$.

Diffusion flows of both components in a binary mixture are equal in magnitude and are opposite in direction.

As already was noted above, diffusion appears when in the gas there are gradients of concentration, pressure, and temperature.*

In a one-dimensional case, gradients of magnitudes are equal to derivatives with respect to x, and vector **i** has one, x-th component, which we will designate simply through i. Diffusion flow is equal to (see [1])

$$i=-\varrho D\left(\frac{d\alpha}{dx}+\frac{k_p}{p}\frac{dp}{dx}+\frac{k_T}{T}\frac{dT}{dx}\right). \tag{7.15}$$

Here D is coefficient of diffusion; k_pD is coefficient of barodiffusion; k_TD is coefficient of thermal diffusion. Dimensionless value k_p is determined purely by thermodynamic properties of the mixture and is equal to [1]**

$$k_p=(m_2-m_1)\,\alpha\,(1-\alpha)\left(\frac{1-\alpha}{m_2}+\frac{\alpha}{m_1}\right)^{***} \tag{7.16}$$

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*State of the binary mixture is characterized by three thermodynamics magnitudes: concentration and any two of the three magnitudes: temperature, pressure, and density. During the study of diffusion, as independent variables it is convenient to select pressure and temperature.

**In the absence of viscous transfer of pulse (see below).

***Magnitude of k_p is the simplest of all to derive, considering equilibrium of the binary mixture in the field of gravity during constant temperature. In equilibrium state numbers of molecules 1 cm^3 n_1 and n_2 by formula of Boltzmann are proportional to $n_1 \sim \exp(-m_1gx/kT)$, $n_2 \sim \exp(-m_2gx/kT)$, where g is acceleration of gravity.

At $m_2 > m_1$ $k_p > 0$ and barodiffusion flow of light component is directed toward lowering. Flow connected with gradient of concentration also is directed toward lowering of concentration. Thermal diffusion flow of light component for a majority of mixtures is directed toward increase of temperature (at $m_2 > m_1$ $k_T < 0$).

In distinction from magnitude k_p, magnitude k_T, called thermal diffusion ratio, depends not only on concentrations of components (at $\alpha = 0$ or 1 $k_T = 0$) and masses of molecules, but also on law of interaction of molecules. Magnitude of k_p is determined purely by thermodynamic properties of gas, since in the field are external forces thermodynamic equilibrium is possible even in the presence of gradient of pressure. If there exists gradient of temperature, then state already is unbalanced.

If between molecules act only repulsive forces, changing according to the law $1/r^n$, then at $n > 5$, which usually takes place, $k_T < 0$: light gas tends toward increase of temperature. At $n < 5$, which is rarely encountered, light gas tends toward lowering of temperature (to the $n < 5$ pertains the Coulomb law of interaction of charged particles, $n = 2$). At $n = 5$ there is no thermal diffusion: $k_T = 0$. Usually during comparable relative gradients $\nabla p/p$, $\nabla T/T$ the role of thermal diffusion is small in comparison with the role of barodiffusion. For greater detail about thermal diffusion see [19].

With diffusion flow is connected additional irreversible energy flow **q**, which is proportional to diffusion flow **i** (see [1]).

Quite recently there appeared a work of V. Zhdanov, Yu. Kagan, and A. Sazykin [19a], which introduces essential corrections to the

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[FOOTNOTE CONT'D FROM PRECEDING PAGE].
x is height. Inasmuch as diffusion flow in equilibrium is equal to zero, $d\alpha/dx + (k_p/p)(d_p/dx) = 0$. Using bond between concentration α and numbers of particles n_1, n_2 and noticing that $p = (n_1 + n_2)kT$, we find hence the given formula for k_p.

above-stated classical presentations on diffusion.

In this work the expression for diffusion flow is derived from kinetic equation with the help of the so-called "13 moments" approximation of Gred. This approximation possesses a number of advantages as compared to the method of Chapman — Enskog, on the basis of which is obtained expression (7.15), every time, when it is necessary to take into account highest approximations in a series of distribution functions. It turns out that expression (7.15) for diffusion flow is accurate only in the absence of viscous transfer of pulse in gas. Under conditions when there exists viscous transfer of pulse (i.e., gradient of speed), expression (7.15) one should supplement with members proportional to the forces of viscosity. In spite of the fact that these forces are determined by derivatives of the second order from macroscopic magnitudes (from speed), they can have the same order of smallness as members proportional to the first derivative, let us say, a member with gradient of pressure. For instance, in the case of purely viscous established flow, when accelerations are lacking, gradient of pressure is simply balanced by forces of viscosity. During transient flow calculation of forces of viscosity in the expression for diffusion flow actually brings to this expression members proportional to the accelerations of gas.

In the case of purely viscous flow, replacement of the force of viscosity by the gradient of pressure balancing it leads to a change in the constant of barodiffusion k_p as compared to purely thermodynamic value (7.16). The constant of barodiffusion in viscous flow is no longer a thermodynamic magnitude; it depends on the character of interaction of the molecules between themselves. The constant of barodiffusion can even become, under certain conditions, negative (if, molecular weights of components differ only slightly, and effective sections of molecules differ strongly). During calculation of viscous transfer of pulse, thermal diffusion ratio k_T changes also.

§ 5. Diffusion in a Shock Wave Spreading Along a Binary Mixture

We will observe what occurs when along a binary mixture of gases spreads a shock wave. In front of the shock wave are large gradients of thermodynamic magnitudes, and, consequently, there appear favorable conditions for diffusion. Physically, it is clear that in front of the shock wave there occurs concentration of the light component. Really, in heated gas after the front of the shock wave the molecules of the light component possess larger thermal velocity than the molecules of the heavy component ($\bar{v} \sim \sqrt{T/m}$).

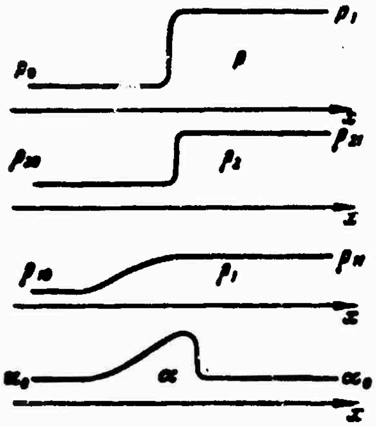

Fig. 7.10. Profiles of pressure and densities of heavy (ρ_2) and light (ρ_1) components and concentrations of light component (α) in a shock wave spreading along a binary mixture of gases.

Therefore, molecules of light gas "burst forward" and somewhat outstrip molecules of heavy gas (in the laboratory system of coordinates, where initial mixture rests).

Let us assume that in heavy gas there is a small impurity of light gas. Then distribution of densities of basic, heavy, and light gases (ρ_2 and ρ_1) in a strong shock wave has the form shown in Fig. 7.10. There depicted is the profile of concentration of the light component: $\alpha = \rho_1/(\rho_2 + \rho_1)$.

Width of the zone in which there is an increased concentration of light component, in order of magnitude is equal to $\Delta x \sim D/u_0$, where D is the coefficient of diffusion, and through u_0 is designated here the speed of the shock wave.* The coefficient of diffusion D of an order of $\bar{l}v_1$, where $\bar{v}_1$ is thermal velocity of light gas heated in the shock wave, and l is range of molecules. Speed of front u_0 of the order of the thermal velocity of the heated heavy gas $u_0 \sim \bar{v}_2$. But $\bar{v}_1/\bar{v}_2 \approx \sqrt{m_2/m_1}$, so that $\Delta x \approx \sqrt{m_2/m_1}\, l$. Width of the viscous shock wave is of the order of l. Consequently, width of the zone of concentration of the light component is $\sqrt{m_2/m_1}$ times more than the width of the shock wave. The sharpest components are most sharply distinguished during great difference in mass of particles ($m_2/m_1 \gg 1$).

This effect should be especially clearly expressed in the case of plasma in view of the huge difference masses of electrons and ions. However, in plasma an essential role is played by the electrostatic interaction of electrons and ions, which very strongly limits the diffusion process (see about this in § 13).

Along with viscosity and thermal conduction diffusion affects the structure of the front of the shock wave. In order to describe this structure, one should compose an equation of flat stationary conditions, just as this was done in § 2, in examining a viscous shock wave. Equations of conservation of mass and momentum, the first and the second of the equations of (7.3), remain, obviously, without changes (under μ now one should understand the coefficient of viscosity of the mixture). In equation of conservation of energy (third of the equations of (7.3)) it is necessary to add molecular flow of heat, connected with diffusion, and instead of molecular flow, caused by thermal conduction S, to write sum of S + q. In system of equations

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*This follows from condition of stationariness of total flux of the light component in the system of coordinates connected with the the front. Approximately $\rho_1 u_0 = D d\rho_1/dx$, whence $\rho_1 = \rho_{11} \exp(-u_0|x|/D)$. Here is used approximated boundary condition, according to which one may assume that at point x = 0, where there is viscous shock wave, density of the light component is equal to its final value ρ_{11}.

now will enter diffusion flow i, to which is proportional flow of heat, q, i.e., will enter new unknown function, concentration α. Therefore, to the system there should be added one more equation. This is the equation of continuity (conservation of mass) of one of the components (in the presence of an equation of continuity for all the mass of gas; preservation of the second component is ensured automatically).

Condition of constancy of flow of mass of light component in a flat stationary case has the form*

$$\rho\alpha u + i = \mathrm{const} = \rho_0\alpha_0 u_0$$

(before the wave diffusion flow disappears). Hence, one should mention, it is clear that after the wave, where diffusion flow also disappears, concentration is equal to initial $\alpha_1 = \alpha_0$ (since $\rho_1 u_1 = \rho_0 u_0$).

System of equations of a one-dimensional stationary flow in a binary mixture, in principle, it is possible to solve just as for single-component gas (see § 2). Solution will give distribution of all magnitudes in front of the wave. Such problem was considered by S. P. D'yakov [20] for the case of a shock wave of weak intensity, when it is possible to produce expansion of all magnitudes (see § 23, gl. I).**

As was shown in § 18 and 23, Chapter I, if one were to consider change of pressure in a weak shock wave $\Delta p = p_1 - p_0$ as a magnitude of the first order of smallness, then change of volume and temperature also constitute small magnitudes of the first order. Full change of entropy during transition of gas from initial state to final $\Sigma_1 - \Sigma_0$

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*General equation of continuity for one of the components has the form [1]

$$\frac{\partial\rho\alpha}{\partial t} + \mathrm{div}\,(\rho\alpha u + i) = 0.$$

**See also work of Sherman [21].

is a magnitude of the third order of smallness, and change of entropy inside front of wave, let us say, $\Sigma_{max} - \Sigma_0$ is a magnitude of the second order of smallness. Width of the front of the shock wave, in order of magnitude, is equal to $\Delta x \approx l p_0/\Delta p$, where l is range of molecules. From equation of preservation of flow of one component, which can be rewritten in form

$$\alpha - \alpha_0 = -\frac{i}{\rho_0 u_0},$$

and expression for diffusion flow, it is clear that change of concentration in wave $\Delta\alpha$ and flow i is a magnitude of the second order of smallness (indeed,

$$\alpha - \alpha_0 \sim i \sim dp/dx \sim \Delta p/\Delta x \sim (\Delta p)^2).$$

Consequently, member containing gradient of concentration in expression for diffusion flow it is possible to disregard ($d\alpha/dx \sim \sim \Delta\alpha/\Delta x \sim (\Delta p)^3$, then as $dp/dx \sim (\Delta p)^2$).

In the work of S. P. D'yakov [20] there is obtained an analytic solution for the distribution of concentration in the front of a shock wave of weak intensity. We will not here introduce it (distribution has the form shown in Fig. 7.11), but we will estimate change of concentration in order of magnitude. If we disregard thermal diffusion, which usually plays a smaller role than barodiffusion (since magnitude of k_T usually is less than k_p), then it is possible to record

$$\Delta\alpha = \alpha - \alpha_0 \sim \frac{|i|}{\rho_0 u_0} \sim \frac{D}{u_0}\frac{k_p}{p}\frac{\Delta p}{\Delta x}.$$

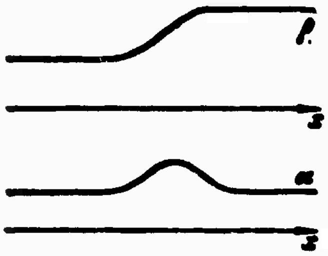

Fig. 7.11. Profiles of density and concentration in a shock wave of weak intensity, spreading along a binary mixture of gases.

Coefficient of diffusion $D \sim \bar{l}v$, where thermal velocity of molecules $\bar{v}$ is of the order of the speed of sound, i.e., of the order of u_0. Noticing that $\Delta x \sim (p/\Delta p)l$, we will find $\Delta\alpha \sim k_p(\Delta p/p)^2$.

Excess quantity of the light component gathered by the shock wave (on 1 cm^2 of surface of front), is of the order of

$$M = \rho \int_{-\infty}^{\infty} (\alpha - \alpha_0)\,dx \sim \rho\,\Delta\alpha \cdot \Delta x \sim \rho k_p \frac{\Delta p}{p} l.$$

In a sufficiently strong shock wave, where $\Delta p \sim p'$, $\Delta\alpha \sim k_p$, $M \sim \sim \rho k_p l$. If difference in mass of molecules is comparatively great ($k_p \sim \sim (m_2 - m_1)$), then change of concentration in a strong wave is of the actual concentration and excess mass of the component is of the order of the actual order of the actual mass of the component in a layer with thickness in the range of molecules.

Above it was noted that diffusion is like viscosity and thermal conduction leads to dissipation of mechanical energy and increase in entropy of the gas (see about this in [1].* We know that if one were to exclude from consideration the dissipative processes, then within the bounds of hydrodynamics of an ideal liquid a shock wave constitutes a mathematical discontinuity. The discontinuity fades out and is turned into a layer of final thickness with continuous distribution of magnitudes only during calculation of dissipative processes. One thermal conduction can ensure continuous transition in shock wave only if the amplitude of the wave is not too great (see § 3).

It is interesting to observe whether dissipation of diffusion origin, without taking into account viscosity and thermal conduction, can ensure continuous transition in a shock wave spreading along a binary mixture. This question was investigated by Cowling [22] (Cowling disregarded thermal diffusion). It turns out that, as in the case of the action of only thermal conduction, continuous solution is possible only during amplitudes of shock wave not exceeding a defined limit,

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*Like thermal conduction diffusion can lead to local decrease of entropy (see § 2). Thanks to diffusion there is increased entropy of all the system on the whole or entropy of a particle for the entire process, let us say, during transition from the initial state to the final in the shock wave. In distinction from thermal conduction and diffusion, viscosity leads to local increase of entropy, i.e., because of viscosity entropy of particle can only increase.

which depends on the difference in mass of molecules and concentration of components. In limiting cases, when concentration of one of the components aspires to zero ($\alpha \to 0$ or $\alpha \to 1$), i.e., when gas is turned into single-component gas, or when relative difference in mass aspires to zero, the upper value of the possible amplitude of the shock wave also aspires to zero. During large difference in mass of molecules and congruent numbers of molecules of both sorts, diffusion ensures continuity of transition up to rather large amplitudes of shock waves, being in this respect more effective than thermal conduction. Thus, for instance, in a mixture of hydrogen and oxygen ($m_1/m_2 = 1/8$) during molar concentration of oxygen (N_2/N), equal to 10%, continuous compression is possible of mixture in shock wave up to 4.78 times (limiting compression at value $\gamma = 7/5$, which was accepted in calculation, equal to 6). One thermal conduction can ensure continuous compression not more than $\frac{3\gamma - 1}{\gamma + 1} = \frac{4}{3}$ times.

2. Relaxation Layer

§ 6. Shock Waves in Gas with Delayed Excitation of Certain Degrees of Freedom

For excitation of certain degrees of freedom of gas* there are frequently required many collisions of molecules, where necessary numbers of collisions, i.e., relaxation times, for various degrees of freedom can differ strongly.

Time of establishment of full thermodynamic equilibrium in the front of the shock wave, and consequently also the width of the front are determined by the slowest of relaxation processes. Of course,

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*Let us remember that for brevity of terminology "degree of freedom" also includes potential energy of dissociation, chemical transformation, and ionization.

one should take into account only those processes which lead to excitation of degrees of freedom giving a noticeable contribution to heat capacity during final parameters of the gas. If τ_{max} is the biggest relaxation time, and u_1 is the speed of gas after the front, with respect to the actual front, then the width of the front is of the order of $\Delta x \sim u_1 \tau_{max} = D(\rho_0/\rho_1)\tau_{max}$.*

"Excited" fastest of all in the gas are forward degrees of freedom of particles. Therefore, machanical energy of the flow of gas incident on the discontinuity, first of all, is turned into energy of forward thermal agitation of atoms and molecules of gas. As was shown in § 2, width of viscous shock wave in strong shock waves is of the order of one or several gas kinetic mean free paths.

During room temperatures, rotation in molecules is excited also fast, as a result of the small number of collisions; oscillations with these temperatures usually do not play a role. Consequently, the width of a front of weak shock waves spreading along molecular gas, heated to room temperature, is of the order of several gas kinetic mean free paths.**

During temperatures of the order of 1000°K, when magnitude of kT is comparable with the energy of vibrational quanta of molecules $h\nu_{vib}$, excitation of vibrations requires many thousand, and sometimes tens and hundreds of thousands of collisions. Width of front of shock wave of corresponding amplitude is determined by relaxation time for vibrational degrees of freedom.

Speeds of relaxation processes always rapidly increase with increase of temperature; thus, for example, temperatures of the order

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*Subsequently, we again will designate speed of the front of the shock wave through D.

**Exceptions are molecular hydrogen and deuterium, in which for excitation of rotations there is required an order of hundreds of gas kinetic collisions (see § 2, Chapter VI).

of 8000°K, when $kT \gg h\nu_{vib}$, for excitation of vibrations even a few collisions are sufficient. Those processes which during any wave amplitude were slow and which determined width of front, in a wave of large intensity become fast, and others arrive to replace them.

For instance, at a temperature of the order of 4000-8000°K in diatomic gas achievement of thermodynamic equilibrium basically is delayed because of slow dissociation of molecules (vibrations are excited comparatively fast, and ionization still is insignificant).

At a temperature of the order of 20,000°K, for dissociation of molecules of a sufficiently small number of collisions, and width is determined by speed of first ionization (second ionization is immaterial). At $T \sim 50{,}000$°K for replacement of first ionization there arrives the second, etc.

Certainly, the boundary of the temperature range in which a relaxation process is slow is not clear. Exactly so at a given temperature not always only one of the processes determines thickness of front. But in any approximation it is always possible for a shock wave of a given amplitude to subdivide processes of excitation of different degrees of freedom, introducing a noticeable contribution to heat capacity, into fast and slow. Under fast we should understand processes for which relaxation times τ_{rel} are comparable to gas kinetic processes and for which characteristic scales $\Delta x = u_1\tau_{rel}$ are of the order of a few gas kinetic mean free paths, i.e., are comparable with thickness of viscous shock wave. The slow ones include processes requiring a very large number of gas kinetic collisions.

The question about the structure of the front of the front of a shock wave in gas with delayed excitation of part of the heat capacity was for the first time analyzed by one of the authors in 1946

[23, 24] in examples of reversible chemical reaction and excitation of vibrations in molecules.

Let us consider qualitatively the process of shock compression in gas with delayed excitation of certain degrees of freedom. We will not, as yet, specify forms of degrees of freedom and will only divide them into two categories: those which are excited fast and those which require many gas kinetic collisions.

Dissipative processes — viscosity and thermal conduction — play a role only in the region of large gradients of hydrodynamic magnitudes, i.e., in the zone where are excited rapidly relaxing degrees of freedom. This zone, in some measure, coincides with the region of viscous shock wave. In the zone of slow relaxation, stretched to distances of many gas kinetic paths, gradients are small and it is possible to disregard dissipation.

We will not be interested in the structure of the narrow zone of fast processes. It, in principle, does not differ from the structure of viscous shock wave considered in § 2. Increase of heat capacity because of fast excitation of nonforward degrees of freedom introduces only certain quantitative changes in the structure of viscous shock without changing basic qualitative regularities. Inasmuch as thickness of this zone is small, of the order of several paths, it is possible, approximately, to consider it as infinitely thin and magnitudes along both sides of it to connect by equations of preservation, fully analogous to equations (7.4). Subsequently, for definitiveness of terminology, we will call the zone of fast relaxation "compression shock" in distinction from the idea of "front of shock wave," which includes all the transition region from initial to final thermodynamically equilibrium state. Marking hydrodynamic magnitudes directly after compression shock by a stroke, we will record equation for determination of these magnitudes

$$\rho' u' = \rho_0 D; \quad p' + \rho' u'^2 = p_0 + \rho_0 D^2; \quad w' + \frac{u'^2}{2} = w_0 + \frac{D^2}{2}.$$

Enthalpy $w' = w'(p', \rho') = w'(T', \rho')$ includes only the rapidly excited degrees of freedom of gas.

Stretched zone of slow relaxation is described by integrals of equations of a one-dimensional stationary flow of type (7.3), in which it is possible to disregard dissipative members.

Considering ρ, p, ε, w, u as functions of current coordinate x, we will record integrals of equations in this zone:

$$\left.\begin{aligned} \rho u = \rho_0 D = \rho' u', \\ p + \rho u^2 = p_0 + \rho_0 D^2 = p' + \rho' u'^2, \\ w + \frac{u^2}{2} = w_0 + \frac{D^2}{2} = w' + \frac{u'^2}{2}. \end{aligned}\right\} \tag{7.17}$$

Origin of coordinates $x = 0$ is convenient to place at a point corresponding to compression shock, which is considered "infinitely thin." Exactly so if one were to trace the change in time of the state of a specific particle of gas passing through the front of a shock wave, then for initial moment $t = 0$ it is convenient to take the moment of sharp compression in the shock wave. Initial or boundary conditions for gas-dynamic parameters $\rho(x)$, $u(x)$, etc., have the form $\rho(0) = \rho'$, $u(0) = u'$, etc. At $x \to +\infty$, as also earlier, $\rho(\infty) = \rho_1$, $u(\infty) = u_1$, etc.

Let us depict on diagram p, V two adiabats of Hugoniot, coming out of point A of initial state of gas (Fig. 7.12). One of them (II) corresponds to achievement of full thermodynamic equilibrium, i.e., corresponds to final states of gas after front of shock wave. The other (I) corresponds to excitation only of rapidly relaxing degrees freedom and the "frozen" nature of the slowly relaxing ones (during calculation of adiabat I it is considered that specific internal energy in slowly excited degrees of freedom is the same as in the initial state, in spite of the fact that density and pressure of gas change).

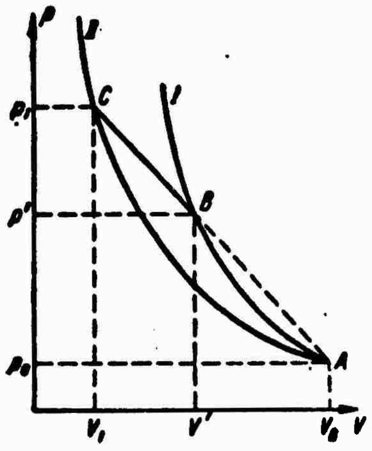

Fig. 7.12. p, V-diagram for a shock wave spreading along gas with delayed excitation of part of the degrees of freedom.

Adiabat I is steeper than II, as was shown in Fig. 7.12. Actually, during identical density, temperature and pressure of gas during the "freezing" of certain degrees of freedom are higher since, roughly speaking, identical energy of compression is distributed among a smaller number of degrees of freedom.*

Let us make straight line AC, connecting initial and final state of gas. As is known, slope of this straight line is determined by speed of propagation of shock wave along unexcited gas D.

From the first two equations of (7.17) it follows that the state of a particle of gas in the relaxation zone changes along this straight line:

$$p = p_0 + \varrho_0 D^2 \left(1 - \frac{V}{V_0}\right) = p' + \varrho' a'^2 \left(1 - \frac{V}{V'}\right). \qquad (7.18)$$

Thus, a point describing the consecutive states of a particle of gas at a given speed of front, by a jump pressure from initial state $A(p_0, V_0)$ to intermediate state $B(p'V')$ after compression shock and then moves to final state $C(p_1, V_1)$ along a straight line (7.18). Pressure and compression increase as it approaches final state, but

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*With this, as calculations show, increase in number of particles during dissociation or ionization does not compensate for decrease of temperature because of expenditures of energy on dissociation and ionization during constant volume, so that pressure in case II is, nevertheless, less than in case I.

speed of gas, with respect to the front, decreases.

If a wave is so weak that the speed of it is less than the speed of sound, corresponding to the frozen nature of part of the degrees of freedom, straight line AC passes below tangent to adiabat I at point A (Fig. 7.13). With this, the state changes continuously along straight line AC from point A to point C, and in the gas, from the very beginning, occurs gradual excitation of the delayed part of heat capacity.

Fig. 7.13. p, V-diagram for a weak shock wave spreading along gas with delayed excitation of part of the degrees of freedom. AK — tangent to shock adiabat I at point A.

From formula (7.18) it is clear that pressure in the relaxation zone in a strong shock wave increases somewhat. Really, even if in the zone of fast compression there are excited only forward degrees of freedom, $V'/V_0 = 1/4$, then pressure, in the relaxation layer can grow not more than 25%, since magnitude $1 - V/V_0$, which is proportional to change of pressure $p - p_0$, is included in interval $1 > 1 - V_1/V_0 > 1 - V'/V_0 >> 3/4$. If, however, other degrees of freedom are fast excited, $V'/V_0 < 1/4$, change of pressure in the relaxation zone is still less. Quite insignificant is the increase of enthalpy in the relaxation region. From the third and first equations of (7.17) it follows that

$$w = w_0 + \frac{D^2}{2}\left(1 - \frac{V^2}{V_0^2}\right). \qquad (7.19)$$

Magnitude $(V/V_0)^2 < 1/16$, so that increase of enthalpy in relaxation zone in any case does not exceed 5-6%.

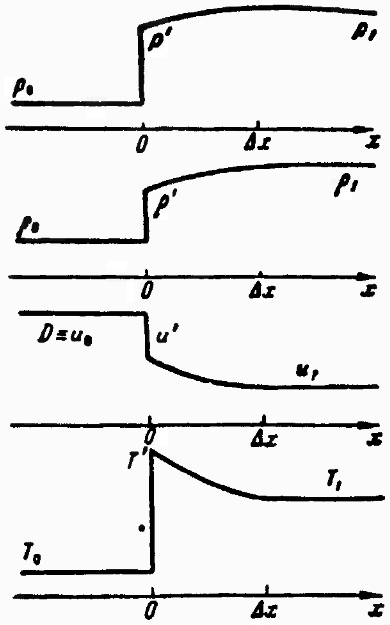

Fig. 7.14. Profiles of pressure, density speed, and temperature in the front of a shock wave spreading along gas with delayed excitation of part of the degrees of freedom; $\Delta x \approx u\tau_{rel}$ is width of front.

Inasmuch as in the relaxation zone specific emthalpy is almost constant, and heat capacity, according to the amount of exitation of earlier frozen degrees of freedom, increases, temperature in it decreases. Decrease of temperature can be quite considerable if the delayed part of heat capacity is large and introduces a large contribution to final heat capacity of the gas. Final temperature T_1 can be two-three times less than temperature T' after compression shock. Exactly so can considerably increase also density of gas (roughly speaking, $p \sim \rho T$; p changes slightly and T strongly). Profiles of p, ρ, u, T in the front of a shock wave spreading along gas with delayed excitation of part of the heat capacity are depicted schematically in Fig. 7.14.

For concrete calculations of profiles one should use equations of kinetics for corresponding relaxation processes, which will be done for several cases in the following paragraphs.

Let us note that if a shock wave is created by a piston moving with constant speed u, then speed of gas after compression shock relative to undisturbed gas D — u' does not coincide with speed of piston (it is less than the latter); with speed of piston coincides only relative speed of gas in final state after front of wave: $D - u_1$.

§ 7. Excitation of Molecular Vibrations

At temperature of the order of 1000-3000°K after the front of the shock wave (depending upon type of molecules), dissociation of molecules is very small, and the contribution of chemical energy to internal energy of the gas it is possible to disregard. Broadening of the front occurs basically because of delayed excitation of molecular vibrations. Rotation of molecules with such temperatures are excited very fast, as a result of several collisions, so that rotary energy in each point of the front of the wave is equilibrium and corresponds to "forward" temperature of gas at this point.

We will consider diatomic gas from molecules of one sort, in the initial state heated to normal temperature of an order of $T_0 \approx 300^\circ K$. With such temperature vibrational energy is exceedingly small and adiabatic index is equal to 7/5. Parameters of gas after compression shock it is possible to calculate with the help of the usual formulas for ideal gas with constant heat capacity corresponding to the participation of only forward and rotary degrees of freedom of molecules and adiabatic index $\gamma' = 7/5$. Let us write out these formulas, characterizing amplitude of shock wave by Mach number ($M = D/c_0$; $c_0^2 = \frac{7}{5} p_0 V_0$), as this is assumed when carrying out laboratory investigations:

$$\frac{\varrho'}{\varrho_0} = \frac{6}{1+5M^{-2}},$$

$$\frac{p'}{p_0} = \frac{7}{6} M^2 - \frac{1}{6},$$

$$\frac{T'}{T_0} = \frac{1}{36} (7 - M^{-2})(M^2 + 5).$$

Parameters of final state, after the front of the shock wave, it is possible to calculate with general relationships on the front, being given by functions $w_1(T_1)$ or $\varepsilon_1(T_1)$ taking into account vibrational energy.

In general the final parameters of the gas are not expressed by simple formulas, since vibrational energy in the quantum region in a complex form depends on temperature (see formula (3.19)). If one were to consider sufficiently strong shock waves in which temperature after the front is larger than energy of vibrational quanta divided by Boltzmann constant, $T_1 > h\nu/k$, then vibrational energy is equal to its classical value kT per molecule and $\varepsilon = \frac{1}{\gamma - 1} p/\rho$, where adiabatic index $\gamma = 9/7$. In this limiting case $\varepsilon_1 = 7/2\, p_1V_1$, shock adiabat has simple form:*

$$\frac{p_1}{p_0} = \frac{6 - V_1/V_0}{8V_1/V_0 - 1} \quad \text{or} \quad \frac{V_1}{V_0} = \frac{p_1/p_0 + 6}{8p_1/p_0 + 1}. \tag{7.20}$$

With the help of general relationship (1.67), from which it follows that

$$\frac{7}{5} M^2 = \frac{p_1/p_0 - 1}{1 - V_1/V_0} \tag{7.21}$$

it is possible to easily express p_1/p_0, just as V_1/V_0 and $T_1/T_0 = p_1V_1/p_0V_0$, through Mach number M.

It is necessary to say that domain of applicability of the shown simple formula for shock adiabat of diatomic gas is very limited. If $T_1 < h\nu/k$, then vibrational energy is not equal to kT; at temperatures noticeably exceeding $h\nu/k$, dissociation of molecules becomes essential.

Let us consider for example a shock wave in oxygen with Mach number M = 7. Let us assume that initial temperature is equal to $T = 300^\circ K$. If initial pressure is atmospheric, speed of sound is equal to $c_0 = 350$ m/sec. and speed of shock wave D = 2.45 km./sec. Parameters of gas after compression shock are equal to $\rho'/\rho_0 = 5.45$, $p'/p_0 = 57$, $T'/T_0 = 10.5$, $T' = 3150^\circ K$.

Parameters in final state after front of wave are: $\rho_1/\rho_0 = 7.3$,

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*We will emphasize that these formulas do not coincide with formulas for gas with constant index $\gamma = 9/7$, since in initial state $\gamma = 7/5$ and $\varepsilon_0 = 5/2\, p_0V_0$.

$p_1/p_0 = 60$, $T_1/T_0 = 8.2$, $T_1 = 2460^\circ K$. For oxygen $h\nu/k = 2230^\circ K$; T_1 a little more than this magnitude, so that a simple formula for calculation of T_1 it is possible to use (dissociation of oxygen with such a temperature and not too small a density is so small that it is possible not to consider it).

Let us find the distribution of parameters of gas in the relaxation zone and we will estimate its width. Specific internal energy of gas at any point x is composed of the energy of forward and rotary degrees of freedom, equal to 5/2 AT, where T is "forward" temperature at point x, and A is constant, calculated per gram, and nonequilibrium energy of vibrations, which we will designate by ε_k : $\varepsilon = \frac{5}{2} AT + \varepsilon_k$. As already was noted above, specific enthalpy practically does not change in relaxation zone (in the given numerical example its change is only 1%), therefore,

$$w = \frac{7}{2} AT + \varepsilon_k \approx \text{const} \approx w_1 \approx w'.$$

This formula connects nonequilibrium energy of vibrations with temperature at point x. Directly after compression shock vibrations are still not excited (in initial state at $T = T_0 \approx 300^\circ K$ vibrational energy is very small), so that at point x = 0 after compression shock $\varepsilon_k = 0$. Then starts gradual excitation of vibrations; ε_k grows, and temperature drops from T' to final quantity T_1, at which vibrational energy attains equilibrium value corresponding to this temperature In order to find distribution of temperature with respect to x, we will use equation of kinetics of excitation of vibrations (6.9):

$$\frac{d\varepsilon_k}{dt} = \frac{\varepsilon_k(T) - \varepsilon_k}{\tau_k}.$$

Here $\varepsilon_k(T)$ is equilibrium energy of vibrations, corresponding to forward temperature T, and τ_k is relaxation time.

We will, for simplicity, consider only sufficiently strong shock waves in which temperature is high and equilibrium vibrational energy is expressed by classical formula: $\varepsilon_k(T) = AT$. With this $\varepsilon_k = w_1 - \frac{7}{2}AT = \frac{9}{2}AT_1 - \frac{7}{2}AT$. Substituting these expressions in equation of kinetics and passing from particle time derivative to differentiation with respect to coordinate, taking into account stationariness of the process: $\frac{d}{dt} = \frac{\partial}{\partial t} + u\frac{\partial}{\partial x} = u\frac{d}{dx}$, we will obtain equation:

$$\frac{dT}{dx} = \frac{9}{7}\frac{T_1 - T}{u\tau_k}.$$

Relaxation time τ_k depends on temperature and density (or pressure) of gas. This dependence it is possible to describe approximately by the formula (6.17), derived in § 4. Chapter VI:

$$\tau_k \approx \frac{\text{const}}{\rho} e^{\text{const}/T^{1/3}}.$$

For the purpose of clarification of the physical side of the matter we will approximately consider magnitude $u\tau_k$ in the relaxation zone as constant and corresponding to a certain average between T' and T_1, ρ' and ρ_1, to values of temperature and density ($u = D\rho_0/\rho$). Such an approximation has meaning since temperature and density change not strongly. Thus, in our numerical example temperature changes by 1.28 times, $T^{1/3}$ — by 1.08 times and density and speed change by 1.34 times.

Integrating the equation for temperature with initial condition T = T' at x = 0 and taking into account the fact that owing to condition $w' = w_1$, $T' = \frac{9}{7}T_1$, we will obtain profile of temperature:

$$T = T_1\left(1 + \frac{2}{7}e^{-\frac{9x}{7u\tau_k}}\right) = T'\left(\frac{7}{9} + \frac{2}{9}e^{-\frac{9x}{7u\tau_k}}\right).$$

Considering that pressure is almost constant ($p \sim \rho T \approx \text{const}$), and temperature changes also not strongly, we will find approximately distribution of density:

$$\rho = \rho_1 - (\rho_1 - \rho')e^{-\frac{9x}{7u\tau_k}} = \rho' + (\rho_1 - \rho')\left(1 - e^{-\frac{9x}{7u\tau_k}}\right). \qquad (7.22)$$

Thus, temperature and density at x → ∞ asymptotically near their final values T_1, ρ_1, where effective width of relaxation zone and front of shock wave is equal, approximately to

$$\Delta x = \frac{7}{9} u \tau_k. \qquad (7.23)$$

Formulas (7.22), (7.23) can serve for experimental determination of time of vibrational relaxation. For this purpose, usually by interferometric method, is measured distribution of density after compression shock and width of front of shock wave (see Chapter IV). For deriving more exact data from experiment the presented simple theory it is possible to definitize, considering quantum dependence of vibrational energy on temperature, changeability of speed u = u(x), etc. A qualitative picture of distributions and the order of width of the front, all of these more precise definitions, of course, do not change.

Table 7.1.

M	D, $\frac{km}{sec}$	T_1^0	ρ_1/ρ_0	$\tau \cdot 10^6$, sec	Δx, cm
		oxygen			
5,95	2,08	2000	6,3	5	0,165
8,0	2,8	3300	7,1	0,8	0,031
		nitrogen			
7,42	2,43	3000	6,55	30	1,11
9,97	3,26	5000	7,14	5	0,23

The presented theory is extended even to vibrational relaxation in polyatomic molecules if the amplitude of the shock wave is such that there are excited only the most low-frequency vibrations.* Calculations and measurement for CO_2 and N_2O gases are in work [25]. In Table 7.1 there are given several values of width of front of shock waves in oxygen and nitrogen, determined by vibrational relaxation (according to measurements of Blackman [26]).

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*In the case of nonlinear polyatomic molecules the numerical coefficient 9/7 in formulas (7.21) and (7.22) it is necessary to replace by 11/9 in accordance with different rotary heat capacity (3/2 k per molecule instead of 1 k).

They are given to pressure after the front $p_1 = 1$ atm. ($\Delta x \sim \tau \sim \sim 1/p_1$), initial temperature $T_0 = 296°$.

The most detailed survey of all theoretical works dedicated to calculating the structure of the zone of vibrational relaxation in the front of a shock wave is contained in article Blythe [57]. There are considered the most varied approximate solutions, and also are presented results of exact solutions of equations, obtained with the help of computers (see also [58]).

We will note several of these experimental works in which is studied vibrational relaxation in the front of a shock wave and are determined corresponding relaxation times and speed of excitation of vibrations. Oxygen was studied in works [59, 60], nitrogen oxide in [61], carbon oxide in [62], carbon dioxide in [63, 64].

§ 8. Dissociation of Diatomic Molecules

At temperatures after the front of a shock wave in diatomic gas of the order of 3000-7000°K there is not yet ionization, vibrations of molecules are excited comparatively fast and broadening of the front of the wave is connected with the slowest relaxation process — dissociation of molecules. Appraisals show that time of vibrational relaxation at shown temperatures is approximately one order less than time of establishment of equilibrium dissociation. Therefore, it is possible approximately to consider vibrational energy at each point of relaxation zone, just as rotary in equilibrium. Parameters of gas after compression shock correspond to intermediate valves of adiabat index $\gamma' = 9/7$ (vibrations during such high temperatures are fully "classic"). It is possible to calculate them by the formulas (7.20) and (7.21).

Noticeable dissociation appears only in sufficiently strong shock waves, so that compression after compression shock is close to limiting, which corresponds to index $\gamma = 9/7$ and equal to 8 (we assume that shock wave spreads along gas heated to normal temperature $T \approx 300^{\circ}K$). Formulas (7.20) and (7.21) are simplified and given approximately

$$\frac{\varrho'}{\varrho_0} = 8, \quad \frac{p'}{p_0} = \frac{49}{40}M^2, \quad \frac{T'}{T_0} = \frac{49}{320}M^2,$$

where M is Mach number.

Parameters of gas after front of shock wave, taking into account dissociation, are not expressed by simple formulas (see § 9, Chapter III); they are not calculated on the basis of general relationships on front.

Let us find the distribution of parameters of gas in the relaxation zone. Specific internal energy of gas, taking into account dissociation of molecules, is equal to (see formula (3.21)):

$$\varepsilon = \frac{7}{2}(1-\alpha)AT + 2\alpha\frac{3}{2}AT + \alpha U = \left(\frac{7}{2} - \frac{\alpha}{2}\right)AT + \alpha U,$$

where U is energy of dissociation of 1 g of gas, and α is degree of dissociation (which can be nonequilibrium).

Inasmuch as already, directly after compression shock, the compression of gas is very great (close to octuple), change of pressure in relaxation zone is small, and change of enthalpy is insignificantly small. Hence it follows that

$$p = A(1+\alpha)\varrho T \approx \text{const} = p' = A\varrho' T', \tag{7.24}$$

$$w = \left(\frac{9}{2} + \frac{\alpha}{2}\right)AT + \alpha U \approx \text{const} = w' = \frac{9}{2}AT'. \tag{7.25}$$

These formulas permit expressing degree of dissociation and density at point x of wave through temperature, or temperature and density through degree of dissociation. Thus, for instance, disregarding α ($\alpha < 1$) as compared to 9, we will find from formula (7.25):

$$\alpha = \frac{9}{2}\frac{A}{U}(T'-T) = \frac{9}{2}\frac{T'-T}{T_{\text{дис}}}, \tag{7.26}$$

where $T_{dis} = U/A$ (for instance, for oxygen $T_{dis} = 59{,}400^\circ$K).

After compression shock at point $x = 0$ there is not yet dissociation $\alpha = 0$ and $T = T'$.

Then starts dissociation; degree of dissociation grows, and temperature, due to expenditures of energy on dissociation, drops. This occurs as long as dissociation does not attain equilibrium value corresponding to temperature of gas.

For finding distributions of parameters with respect to x we will use an equation of the kinetics of dissociation (see § 5, Chapter VI).

Let us consider here shock waves of not very great amplitude, in which the degree of dissociation obtainable after the front is small: $\alpha_1 \ll 1$. In this case it is possible to disregard dissociation of molecules by blows of atoms and to leave in equation of kinetics (6.21) only members corresponding to dissociation by blows of molecules and recombination of atoms in triple collisions with the participation of molecules as third particles. During transition in equation of kinetics (6.21) from numbers of atoms in cm^3 to degrees of dissociation by the formula $N_A = 2\alpha N^\circ$ (N° is number of initial molecules in cm^3), one should differentiate with respect to time only the degree of dissociation, but not the density of gas (i.e., N°), since in equation (6.21) there is no member describing density change. If we add such a member, then it will be reduced with component $2\alpha\frac{dN_0}{dt}$, obtained during differentiation of N° in expression

$$N_A = 2N^\circ\alpha.)$$

Disregarding in all members magnitude of α as compared to unity, considering determination of time of relaxation τ (6.25), and passing from particle time derivative to derivative with respect to coordinate, we will record equation of kinetics in the form

$$\frac{d\alpha}{dx}=\frac{(\alpha)}{2u\tau}\left[1-\frac{\alpha^2}{(\alpha^2)}\right],$$

where (α) is equilibrium degree of dissociation, corresponding to temperature and density of gas at point x (see formula (6.23)).

As also in the preceding paragraph, we will consider relaxation time $\tau(T, \rho)$ and speed of gas with respect to compression shock $u = D\rho_0/\rho$ as constants and corresponding to certain mean values of temperature and density in the relaxation zone. If final degree of dissociation is very small, change of temperature and density is not very great, and for the purpose of rough estimate such an approximation is possible to make. Equilibrium degree of dissociation (α) which depends on T and ρ, also we will consider constant and equal to degree of dissociation in final state α_1. Integrating with these assumptions the equation of kinetics and subordinating the solution to initial condition $\alpha = 0$ at $x = 0$, we will obtain

$$\frac{\alpha_1-\alpha}{\alpha_1+\alpha}=e^{-\frac{x}{u\tau}}. \qquad (7.27)$$

If one were to substitute degree of dissociation α calculated by this formula in expression (7.26), we will find profile of temperature T(x) (at $\alpha = \alpha_1$, $T = T_1$), and then by the formula (7.24) we will find profile of density $\rho(x)$. We will not extract formulas for distributions T(x) and $\rho(x)$. It is clear that they, just as formula (7.27), testify to the asymptotic tendency of these magnitudes toward final values after front of the wave T_1 and ρ_1. Effective width of relaxation zone and the front, as one should have been led to expect, is equal to approximately

$$\Delta x \approx u\tau.$$

where τ is certain average relaxation time in nonequilibrium zone.

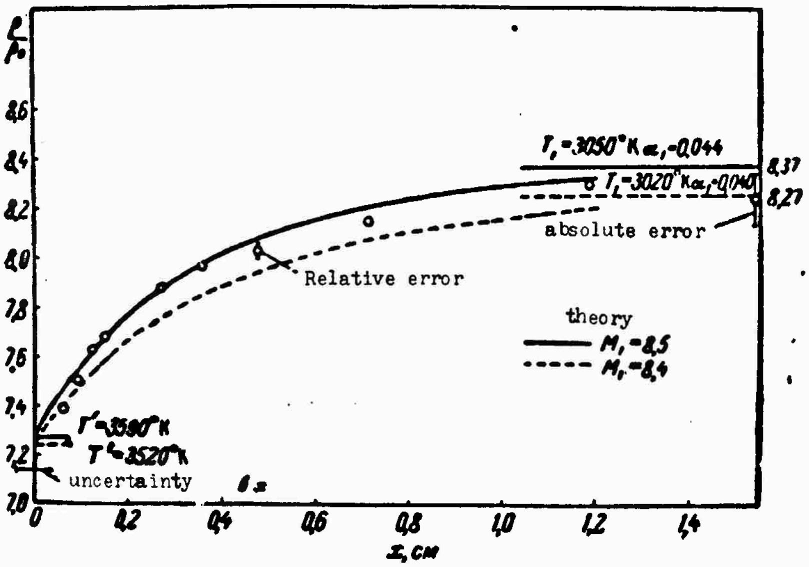

Fig. 7.15. Distribution of density after compression shock in oxygen according to [27]. Initial pressure $p_0 = 19.6$ mm Hg, initial temperature $T_0 = 300°K$.

Nonequilibrium dissociation in the front of the shock wave by experiment was studied by many authors. A whole series of works is dedicated to oxygen. Matthews [27], by interference method, measured distribution of density in nonequilibrium zone after compression shock in a shock tube. Experimental data were compared with theoretical calculations carried out on the basis of a solution of an equation of kinetics of dissociation. There was calculated a number of profiles with different values of constants, entering in the expression for speed of reaction, and constants were chosen so that, best agreement with experiment be received. Calculations of profiles were made more exactly than this was presented above).

The speed of dissociation of oxygen obtained from the experiment, was given in § 6, Chapter VI. In Fig. 7.15 is depicted the profile of density in nonequilibrium zone of a shock wave in oxygen according to Matthews. From Fig. 7.15 it is clear that width of the front of a shock wave, in experimental conditions, is of the order of Δx ≈ 1 cm. S. A. Losev [28] and N. A. Generalov and S. A. Losev [29] measured distribution of temperature after compression shock in zone of nonequilibrium dissociation of oxygen with respect to absorption of ultraviolet radiation in Schumann — Runge bands of molecules of O_2, which depends on temperature. With respect to absorption of light was studied the speed of dissociation of bromine and iodine in a shock wave [30]. Reference to many works can be found in review [31].

Recently there appeared experimental works of Camac [65], Rink, and others [66] in which was studied dissociation of oxygen in a shock wave, work [67], in which was investigated dissociation of hydrogen; in work [68] was studied dissociation and recombination of nitrogen.

§ 9. Shock Waves in Air

Air constitutes a mixture of two diatomic gases: nitrogen and oxygen (79 and 21% in number of molecules). In shock waves, whose amplitudes correspond to final temperatures $T_1 \sim 3000\text{-}8000^\circ K$, there is observed a considerable expansion of the front of the shock wave due to dissociation of molecules of nitrogen and oxygen. Besides reactions of dissociation, in heated air there occurs the reaction of oxidation of nitrogen. Definition of profiles of gas-dynamic magnitudes in the front of a wave and the width of the front requires joint solution of equations of kinetics of all these reactions.

Such calculations were made by Duff and Davidson [32], and also by a number of other authors. A number of works are dedicated to the experimental study of nonequilibrium zone in air with the help of shock tubes. References to these works can be found in review [31].

We will give, for illustration, results of calculations [32] (calculations were made with an electronic computer). In calculations were taken into account the following basic chemical reactions:

$$O_2 + M \rightleftarrows O + O + M,$$
$$N_2 + M \rightleftarrows N + N + M,$$
$$NO + M \rightleftarrows N + O + M,$$
$$O + N_2 \rightleftarrows NO + N,$$
$$N + O_2 \rightleftarrows NO + O.$$

In all these reactions M corresponds to any atom or molecule. For three reactions of dissociation were accepted the following constant values of recombination rates: $3 \cdot 10^{14}$, $3 \cdot 10^{14}$ and $6 \cdot 10^{14}$ $\text{mole}^{-2} \cdot \text{cm}^{6} \cdot \text{sec}^{-1}$. Speeds of straight fourth and fifth reactions were taken in the form

$$k_4 = 5 \cdot 10^{13} \exp\left(-\frac{75500}{RT}\right) \text{ mole}^{-1} \cdot \text{cm}^{3} \cdot \text{sec}^{-1},$$
$$k_5 = 1 \cdot 10^{11} T^{\frac{1}{2}} \exp\left(-\frac{6200}{RT}\right) \text{ mole}^{-1} \cdot \text{cm}^{3} \cdot \text{sec}^{-1}$$

(compare with data in § 8, Chapter VI).

Calculations were conducted on two assumptions: 1) vibrational degrees of freedom at every point of the nonequilibrium zone are equilibrium degrees of freedom, 2) the kinetics of excitation of vibrations were calculated simultaneously with the kinetics of chemical reactions. Distributions of temperature and density after compression shock in a shock wave with Mach number M = 14.2, spreading along air with p_0 = 1 mm Hg, T_0 = 300°K are shown in Fig. 7.16. Temperature after compression shock T' is equal to 9772°K if it is considered that in the discontinuity are excited equilibrium vibrations, and 12,000°K – without taking into account vibrations.

Curves of the first calculation are solid lines, of the second are dotted. Divergence of curves is not very great but still noticeable since speeds of chemical reactions not very greatly exceed speed of excitation of vibrations. Width of front of wave is shown conditions, as can be seen from Fig. 7.16, is of the order of 5 mm.

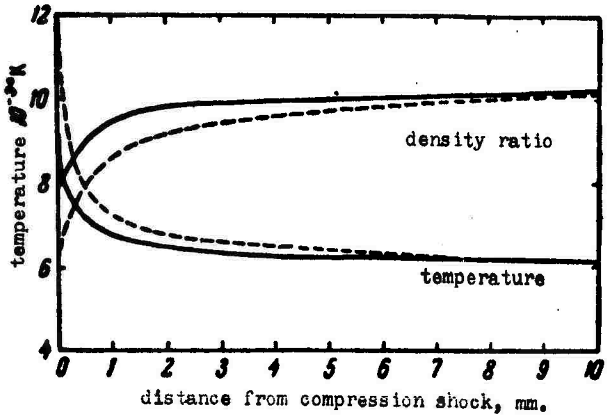

Fig. 7.16. Profiles of temperature and density in the front of a shock wave in air with Mach number M = 14.2. Along the axis of ordinates are temperatures and density ratio ρ/ρ_0. Initial pressure P_0 = 1 mm Hg, temperature T_0 = 300°K. Solid curves correspond to instantaneous excitation, and dotted curves to terminal velocity of excitation of vibrations.

Width of relaxation layer in air in the region of dissociation was measured by N. A. Generalov and S. A. Losev [33]. Change of temperature in relaxation layer was recorded with respect to change of absorption of light from outside source in Schumann — Runge bands of molecules of oxygen. Pressure after the front of the shock wave was close to atmospheric. At D = 3.7 km/sec $\Delta x \approx$ $\approx$ 0.5 cm (average temperature in layer $\bar{T} \approx 4500$°K); at D = 2.8 km/sec Δx = 1.3 cm ($T \approx 3200$°K). Comparison with calculations of Duff and Davidson, above-stated, testifies to correctness of selection of basic constants of speeds of reactions in these calculations.

In one of the last of the works (Wray, Teare, Hammerling, Kivel [69]) there is presented a list of constants of speeds of chemical reactions occurring in heated air. Constants are selected by authors on the basis of analysis of available experimental material and are recommended by them for calculations of nonequilibrium processes in shock waves. Calculations of the structure of the front for air, carried out by the authors, will agree with measurements of Lin [70] in a shock tube.

We will give this list. In the latter of the two lines are given constants of speed of reactions of ionization and recombination of electrons, which play the most important role in the establishment of equilibrium ionization in air at comparatively low temperatures.

Reaction	Constant of recombination rate, cm^6/mole$^2\cdot$sec	Third particle
$O+O+M \rightarrow O_2+M$	$2{,}2\cdot 10^{20}T^{-3/2}$	O
	$8{,}0\cdot 10^{19}T^{-3/2}$	O_2
	$2{,}5\cdot 10^{15}T^{-1/2}$	N_2, N, NO, A
$N+N+M \rightarrow N_2+M$	$5{,}5\cdot 10^{20}T^{-3/2}$	N
	$2{,}0\cdot 10^{20}T^{-3/2}$	N_2
	$6{,}0\cdot 10^{15}T^{-1/2}$	O_2, O, NO, A
$N+O+M \rightarrow NO+M$	$2{,}0\cdot 10^{21}T^{-3/2}$	NO, O, N
	$1{,}0\cdot 10^{20}T^{-3/2}$	O_2, N_2, A
	Constant of speed, cm^3/ mole$\cdot$sec	
$NO+N \rightarrow O+N_2$	$1{,}3\cdot 10^{13}$	
$NO+O \rightarrow N+O_2$	$1{,}0\cdot 10^{12}T^{1/2}e^{-3120/T}$	
$N+O \rightarrow NO^{+}+e$	$3\cdot 10^{12}T^{-1/2}e^{-31715/T}$	
$NO^{+}+e \rightarrow N+O$	$1{,}8\cdot 10^{21}T^{-3/2}$	

Constants of speeds of inverse processes for chemical reactions it is possible to express through constants of speeds of forward processes and corresponding equilibrium constants.

Let us note works [71-75], in which are studied relaxation layer in a shock wave in air and adjacent questions.

§ 10. Ionization in a Shock Wave (Theory)

At temperatures after the front of a shock wave of the order of 15,000-20,000°K gas is noticeably ionized. Establishment of ionization equilibrium with such temperatures is the slowest of relaxation processes and namely it determines the width of the front of the wave.*

From the point of view of the experimental study of ionization in shock tube are particularly attractive monatomic gases such as argon. Thanks to the absence of a number of degrees of freedom which molecular gases possess, in monatomic gases more easily are attained high temperatures ~15,000-20,000°K. Monatomic gases are favorable also for checking the theory of the phenomenon since ionization (first)

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*Dissociation of molecules with such temperatures occurs very fast, as a result of small number of collisions.

is a natural relaxation process expanding the front of the shock wave.

Let us consider a shock wave in monatomic gas. Noticeable ionization is obtained only during very great amplitude of wave; therefore, in the shock wave there is attained limiting compression equal to four, in accordance with adiabatic index $\gamma = 5/3$. Parameters after the compression shock are expressed through Mach number by the simple formulas:

$$\frac{\varrho'}{\varrho_0}=4, \quad \frac{p'}{p_0}=\frac{5}{4}M^2, \quad \frac{T'}{T_0}=\frac{5}{16}M^2. \tag{7.28}$$

For instance, at Mach number $M = 18$ and initial temperature $T_0 = 300^\circ K$, which corresponds to speed of shock wave $D = 5.75$ km/sec, temperature after compression shock $T' = 30{,}000^\circ K$. In equilibrium, after the front of a shock wave in argon, at initial pressure $p_0 = 10$ mm Hg, gas turns out to be ionized approximately 25%, and temperature $T_1 = 14{,}000^\circ K$.

Width of compression shock is equal to approximately two-three gas kinetic mean free paths of atoms. Directly after compression shock gas is not ionized. After shock compression, in highly heated particles of gas ionization starts. As is known, the basic mechanism of ionization in gases not too low in density is ionization by electron blow (see Chapter VI). However, in order that ionization be developed by means of electron blows with the formation of an electron avalanche, it is necessary that in the gas there be a certain initial "startup" quantity of electrons. One of the basic mechanisms which can lead to this initial ionization is ionization during collisions of atoms with each other. As was marked in Chapter VI, the effective section of such a process is extraordinarily small. Therefore, for forming "startup" electrons rather considerable time is required.

Correspondingly, the zone after compression shock, where parameters of gas correspond to an insignificantly small degree of ionization, i.e., are equal to ρ, p', T', extends a very large distance.

Avalanche-type ionization starts when speed of ionization by electron impact becomes more than speed of ionization by impacts of atoms. Inasmuch as the latter is extraordinarily small, avalanche-type ionization starts with very little "priming" when degree of ionization $\alpha \sim 10^{-5} - 10^{-3}$ (depending upon density and temperature of gas; see § 11, and 13, Chapter VI). Let us leave awhile the question on formation of "startup" electrons and let us consider the basic process of ionization by electron impact, as a result of which the degree of ionization grows from very small to equilibrium values ($\alpha_1 = 0.25$ in the above mentioned example).

During constant electron temperature T_e, avalanche grows by exponential law of the type $n_e \sim \alpha \sim e^{t/\tau}$ (see § 11, Chapter VI) until recombination starts noticeably to compensate for ionization. After that the degree of ionization gradually nears to equilibrium, at which recombination accurately compensates for ionization.

Actually, development of the avalanche occurs in a more complex form. The fact is that in each ionizing event electron gas loses energy equal to ionization potential I (which in argon is equal to 15.7 ev). Temperature of electron gas is of the order of 10,000°K, i.e., thermal energy of one electron of the order of 1.5 ev. Thus, on the formation of one new electron is expended energy equal to the thermal energy of approximately then electrons. If thermal energy of the electrons is not complete, electron temperature falls fast. Together with it would fall also speed of ionization, which very sharply, by Boltzmann law e^{-I/kT_e}, depends on electron temperature (see § 11, Chapter VI).

Losses of energy of electrons on ionization are replenished thanks to transmission to the electrons of energy from atomic gas heated in the compression shock. However, exchange of energy between heavy particles and electrons due to a large difference in their masses occurs extremely slowly, and namely this process of exchange limits speed of development of electron avalanche and determines time of achievement of equilibrium ionization.

During a very small degree of ionization, ions are few, and electrons obtain energy during collisions with neutral atoms. But effectiveness of such collisions at electron temperature $T_e \sim 1$ ev $\approx 10^4$ °K is approximately 10^3 times less than the effectiveness of collisions of electrons with ions. Therefore, even at small ionization $\alpha \sim 10^{-3}$ a basic role is played by energy exchange between ions and electrons. Ions have a temperature coinciding with temperature of atoms since, due to identity of masses, energy exchange between atoms and ions is carried out very fast. Thus, a small quantity of ions in given condition serves, as it were, as an intermediary during energy transfer from atoms to electrons. In electron gas itself energy is distributed quickly so that it is possible to speak about electron temperature T_e, which, naturally, differs from temperature of heavy particles — atoms and ions T. Electrons not only ionize but also excite atoms. Energy of the first excited level of an argon atom is equal $E^* = 11.5$ ev. The fate of excited atoms can be different. Excited atoms partially de-excite their energy. Quantum appearing as a result of de-excitation is absorbed by another, nearby, unexcited atom (effective absorption cross section of resonance quanta is very large), which in turn is de-excited, etc.*

During great density of electrons, exceeding approximately 10^{17} cm^{-3}, excited atoms are deactivated basically by electron impacts of the second kind. With this, excitation energy anew returns to electron gas. There is possible also such a process: a fast electron whose energy exceeds the difference between ionization potential and excitation energy I-E*, i.e., binding energy of an excited electron in an atom, knocks out an electron from an atom.

Ionization with this occurs, as it were, in two steps: in the first act an electron excites an atom, and in the second another electron ionizes an excited atom. With such a two-stage process the expenditure of energy on the formation of one new electron also is equal to ionization potential $(I = E^* + (I - E^*))$, as also in single-stage. It is necessary to say that equilibrium degree of excitation of atoms is established very fast, much faster than equilibrium ionization.

We will compose now fundamental equations which describe the process of ionization after a compression shock and profiles of gas-dynamic magnitudes. If α is degree of ionization, U is ionizing energy of 1 g of gas, and T and T_e are temperatures of atoms and electrons, then specific internal energy and enthalpy of gas, on the assumption that degree of ionization is small ($\alpha \ll 1$), can be approximately recorded

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*Resonance quanta, generated in the heated zone after the front of the shock wave, diffusing through the gas and penetrating through the surface of the front, emerge beyond the limits of the heated region. After that they diffuse in undisturbed gas, outstripping propagation of the shock wave. Thanks to diffusion of resonance radiation before the front, at large distances there appears a noticeable concentration of excited atoms. This process was considered L. M. Biberman and B. A. Veklenko [34]. They showed that at a distance of 1 m from the front of a wave in argon with p_0 = 10 mm Hg, M = 18, T_1 = 14,000°K, concentration of excitation of atoms reaches $5 \cdot 10^{13}$ cm^{-3}, which corresponds to a "temperature" of excitation of ~13,500°K, only a little lower than temperature of resonance radiation outgoing from the surface of the front and equal to T_1.

$$\varepsilon = \frac{3}{2}AT + \frac{3}{2}A\alpha T_e + \alpha U \approx \frac{3}{2}AT + \alpha U,$$

$$w = \frac{5}{2}AT + \frac{5}{2}A\alpha T_e + \alpha U \approx \frac{5}{2}AT + \alpha U.$$

Pressure of gas in that same approximation is equal to $p = A\rho T + A\alpha\rho T_e \approx A\rho T$.

From approximate condition of constancy of enthalpy in the relaxation zone there follows a connection of degree of ionization with atomic temperature, analogous to (7.26):

$$\alpha = \frac{5}{2}\frac{A}{U}(T' - T) = \frac{5}{2}\frac{T' - T}{T_{\text{ион}}},$$

where $T_{\text{ion}} = U/A = I/k$ (in argon $T_{\text{ion}} = 1.82 \cdot 10^{5}$ °K). Density ρ it is possible to express through temperature from equation of straight line (7.18) or, approximately, considering $p = A\rho T \simeq \text{const}$. Equation of kinetics of ionization it is possible to record in the form

$$\frac{d\alpha}{dt} = \left(\frac{d\alpha}{dt}\right)_e + \left(\frac{d\alpha}{dt}\right)_a = f_e(\alpha, T_e, \rho) + f_a(T, \rho), \tag{7.29}$$

where first component corresponds to ionization by electron impact, and the second describes initial "startup" ionization by impacts of atoms (and by means of other mechanisms if such exist; see below). As soon as any noticeable quantity of electrons is formed, the first member becomes larger than the second and the equation of kinetics is turned into an equation of avalanche-type ionization. Function f_e was plotted in § 11, Chapter VI. In the shock wave $\frac{d\alpha}{dt} = u\frac{d\alpha}{dx}$.

For determination of electron temperature, on which depends speed of ionization by electrons, there serves equation of balance of electron energy. If one were to designate by Σ_e, $w_e = \frac{5}{2}A\alpha T_e$, $p_e = A\alpha\rho T_e$ entropy and enthalpy of electrons, calculated per 1 g of gas and pressure of electrons, then it is possible to record

$$\rho u T_e \frac{d\Sigma_e}{dx} = \rho u\left(\frac{dw_e}{dx} - \frac{1}{\rho}\frac{dp_e}{dx}\right) = \omega. \tag{7.30}$$

where resultant energy release in electron gas per 1 cm^3 in 1 sec. ω is composed of inflow of heat thanks to energy exchange between atomic (ionic) and electron gases ω_{ea} and losses of energy by electrons on ionization ω_i: $\omega = \omega_{ea} - \omega_i$. The first magnitude, according to formula (6.105), is equal to

$$\omega_{ea} = \frac{3}{2} k \left(\frac{dT_e}{dt}\right)_{ex} n_e = \frac{3}{2} k n_e \frac{T - T_e}{\tau_{ea}}, \tag{7.31}$$

where τ_{ea} is characteristic time of exchange, determined by formula (6.104): $\tau_{ea} \approx \text{const}\ T_e^{3/2}/n_e$($n_e$ is number of electrons in 1 cm^3). Losses of energy on ionization are equal to

$$\omega_i = I\left(\frac{dn_e}{dt}\right)_{\text{ion}} = UQ\left(\frac{d\alpha}{dt}\right)_e = UQu\frac{d\alpha}{dx}. \tag{7.32}$$

Extracted equations also determine the kinetics of the development of an electron avalanche and the distribution of all magnitudes with respect to x in the relaxation zone. It is necessary to note that rate of exchange and nonelastic losses to a considerable degree compensate one another (in electron gas is established a quasi-stati nary state): $\omega = \omega_{ea} - \omega_i \ll \omega_{ea}, \omega_i$.

The equation of balance of electron energy during this it is possible to record approximately in the form

$$\omega = \omega_{ea} - \omega_i = 0,$$

as this is done in the work of Petschek and Byron [35], which theoretically and experimentally studied ionization in a shock wave in argon. Speed of ionization $d\alpha/dt = u\ d\alpha/dx$ then is determined simply as function T_e, ρ and α.

Regarding initial stage of ionization , when degree of ionization is still too small for an avalance to appear, then here position is very indefinite, since effective sections of ionization by impacts of atoms are unknown. However, if one were to be given to some section, then it is possible to produce an entire calculation of kinetics of ionization starting from moment $t = 0$ or from point $x = 0$ after compression shock, in which $\alpha = 0$, and up to achievement of equilibrium.

Calculations on presented program were carried out by Bond [36] for a shock wave in argon initial pressure $p_0 = 593$ mm Hg (equal to atmospheric pressure in Los Alamos) and $T_0 = 285$°K. Equations of the kinetics of ionization,* balance of electron energy, and hydrodynamics were integrated numerically.

For calculation of initial ionization of argon during collisions of atoms with each other, Bond [36] extrapolated to low energies effective sections of ionization Ar-Ar, obtained in works of Rostagni [37] and Wayland [38]. Effective sections corresponding to energy of atoms of the order of I · 1 ev, accepted in the calculation of Bond has an order of $4 \cdot 10^{-21}$ cm^2.**

In Fig. 7.17 are shown profiles of temperature of atoms, density, and degree of ionization for several values of speed of shock wave.

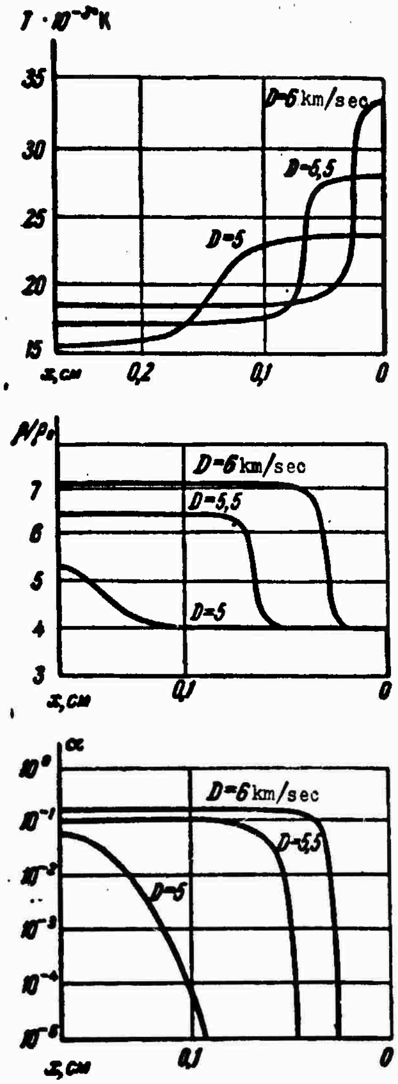

Fig. 7.17. Profiles of temperature of atoms, density, and degree of ionization in the front of a shock wave in argon for three values of speed of front D. In undisturbed gas $P_0 = 593$ mm Hg, $T_0 = 285$°K (graphs are taken from work [36]).

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*In the equation of kinetics of ionization there was considered also recombination, without which the degree of ionization does not aspire to equilibrium value.

**These values are not presented in the work of Bond; however, it is possible to extract them from results of calculation of profiles.

As we see, after the compression shock there spreads a wide region where there is practically no ionization (where is stored "startup" quantity of electrons) and parameters of gas are equal to their own values after the compression shock (ionization degree of freedom is frozen). When α attains magnitude $\sim 10^{-5}$, an avalanche is developed, and all magnitudes "rush" to their final equilibrium values.

It is necessary to note that in spite of the uncertainty in the selection of an effective section of ionization by blows of atoms, the width of the region of accumulation of "startup" electrons has a correct order, since it weakly depends on the section and is determined basically by the scale of time of formation of the avalanche.

In the case T_e = const, time of accumulation of "startup" electrons does not at all depend on effective section, as was shown at the end of § 13, Chapter VI, and is determined only by time of development of avalanche.

§ 11. Ionization in a Shock Wave (Experimental Results; Remarks about Initial Ionization; Air)

Experimental investigation of the establishment of ionization equilibrium in the front of a shock wave in argon was conducted by Petschek and Byron [35]. For this purpose the authors used a shock tube. In order to expand the nonequilibrium region of the front and to increase time of achievement of equilibrium, after making them accessible for measurements, initial pressure of gas was selected comparatively low: $p_0 = 10$ mm Hg. With such densities and speeds of shock wave of the order of 4-5 km./sec. times of relaxation were $\sim 10^{-5}$ sec. and widths of front ~ 1 cm. Distribution of electron density in the front of the wave was measured by two methods: by radiation of continuous spectrum of glow and with the help of probes.

Continuous spectrum appears as a result of recombination of electrons with ions and, consequently, intensity of volume of glow in a given section x of front of shock wave is proportional to square of density of electrons.

Glow was recorded by photomultiplier, current from which was given on an oscillograph. Form of oscillograms was in qualitative agreement with theoretical calculations of degree of ionization in nonequilibrium zone.

Second method, the probe method, allowed to determine gradients of electron density similarly to the usual investigations in gas discharges. Thanks to the existence of a gradient of electron density and the sharp excess of speed of electrons over speed of ions there occurs separation of charges, polarization, and electrical fields appear. The field in ionized gas is shielded at distances of the order of Debye length; therefore, electrons cannot depart from ions to great distances. In experimental conditions Debye length was considerably less electron path. Separation of electrons occurred very fast, as compared to rate of change of electron density, and was always stationary (relative velocity of electrons and ions is equal to zero).

In this case gradient of electron pressure is balanced by electrical field ($\nabla p_e = - n_e eE$), appearing as a result of polarization, for measurement of which into the gas is introduced a probe. Probe measurements of distribution of electron density agreed with measurements by glow and with theory of electron avalanche, restrained by delayed exchange of energy between ions and electrons.

The authors especially investigated the initial stage of ionization, in which are formed "startup" electrons. Comparison of experimental data about the distribution of electron density with the theory of electron avalanche showed that avalanche is developed only after initial ionization attains magnitude of the order of 0.1 from equilibrium, i.e., $\alpha \sim 10^{-2}$. Initial ionization can be connected with impacts of atoms and photo-ionization with quanta being generated as a result of photo-recombination in the equilibrium zone. According to appraisals, photo-recombination in experimental conditions did not play a role. The experiment testifies to the important role played by impurity in the process of initial ionization. Speed of initial ionization strongly depends on degree of purification of argon. However, it is much larger than this is possible to obtain on the basis of appraisals.

Possibly, for initial ionization the diffusion of electrons, the penetration of free electrons in neutral gas from a region of strong ionization, has some value. To the study of the diffusion of electrons in a shock wave are dedicated works [39, 76, 77]. The question about the mechanism of initial ionization as yet remains not fully clear.

Let us give certain results of the measurement of the time of ionization relaxation in argon, obtained in work [35]. Relaxation times and approximate widths of fronts are given to initial pressure $p_0 = 10$ mm Hg (they are inversely proportional to density of gas). Values pertain to very pure gas, with allowance of impurities $\sim 5 \cdot 10^{-5}$

M	$T'°$, K	D, km/sec	$\tau \cdot 10^6$ sec	Δx, см
10,3	10 000	3,3	100	~6,5
11,5	12 500	3,7	17	~1
13,4	16 700	4,3	3	~0,2
16,4	25 000	5,25	0,5	~0,032
20,3	40 000	6,5	0,1	~0,006

Experiment shows that $\ln \tau$, roughly speaking, linearly depends on $1/T'$, i.e., that $\tau \sim \exp(\mathrm{const}/T')$.

Ionization in the front of the shock wave in air was studied in works [40, 70, 78, 79, 80] (see also [41]). In waves of comparatively small amplitude, after whose front degree of ionization is very small, the mechanism of ionization of air essentially differs from the mechanism of ionization of air essentially differs from the mechanism of ionization in monatomic gases. Free electrons are formed basically as a result of reaction N + O $\longrightarrow$ NO^+ + e, which requires small expenditure of energy, only 2.8 ev. Inasmuch as ionization potentials of all components of heated air are considerably larger than this magnitude, the shown reaction at low temperatures occurs much faster than direct processes of ionization of molecules and atoms by impacts of particles.

Constant of speed of this reaction is given in table § 9 (see also § 15, Chapter VI). Calculations of the kinetics of ionization, carried out in the work of Lin and Teare [86] with this value, agree well with experimental data [87], obtained with the help of a shock tube. As shown by experiments and calculations, at speeds of shock wave 4.5-7 km./sec. and initial pressures of 0.02-0.2 mm Hg, ionization after compression shock is developed very fast, at a distance of 40-10 gas kinetic mean free paths, corresponding to unexcited air. With this, maximum degrees of ionization in relaxation layer, which $\sim 10^{-3}$, several times exceed equilibrium values corresponding to final state.

In sufficiently strong shock waves, at high temperatures and noticeable degrees of ionization in air, as also in monatomic gases, to the first plan comes forward ionization by electron impact. Reaction N + O $\rightarrow$ NO^+ + e serves one of the sources of startup needed for the development of an electron avalanche.

One of the most characteristic properties of ionized gases is their ability of conduct electrical current. To the calculations and experimental study of electrical conductivity of ionized air (and other gases) have been dedicated a rather large number of works. See, for instance, [70, 81-84].

§ 12. Shock Waves in Plasma

Interesting peculiarities are possessed by the structure of fronts of shock waves spreading along ionized gas. These peculiarities were marked by one of the authors [42]; quantitative calculations of the structure of a front were done by V. D. Shafranov [43]; see also the work of V. S. Imshennik [51], Jukes [44] and Tidman [44, 44a], S. B. Pikel'ner [85]. Basic features of the structure are connected with the delayed character of energy exchange between ions and electrons and great mobility of electrons, thanks to which electron thermal conduction many times exceeds thermal conduction of ions.

Maxwellian distributions in electron and ionic gases are established very fast, during the order of time between "collisions" of particles.* Levelling of temperatures of both gases, due to the huge difference in mass of electrons and ions, occurs much more slowly. This relaxation process also determines width of the front of a shock wave in plasma.

Let us clarify qualitatively, to what leads the small rate of energy exchange of electrons and ions, for which we will assume at first that electron thermal conduction does not differ from ionic. Furthermore, we will consider that ionization occurs not in the actual shock wave, but the wave spreads along already ionized gas.

In the system of coordinates, connected with the wave, a considerable part of the kinetic energy of the gas, incident on the compression shock, under the action of forces of ionic viscosity, irreversibly passes into heat. Increase of ionic temperature in the shock wave in

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*About the idea of "collision" of charged particles, interacting by Coulomb law, see § 16, Chapter VI.

order of magnitude is equal to $\Delta T_i \sim m_i D^2/k$, where m_i is mass of the ion, and D is approach stream velocity equal to the speed of the front of the shock wave. Thickness of viscous discontinuity is determined by the time between ionic collisions τ_i; it is of the order of the range of ions $l_i \sim \overline{v}\tau_i$, where $\overline{v} \sim D$ is thermal velocity of ions in the compression shock (definition of τ_i is given in § 16, Chapter VI). During compression τ_i ionic gas does not succeed in transmitting to electron gas any noticeable thermal energy since characteristic time of exchange $\tau_{ea} \sim \sqrt{m_i/m_e} \cdot \tau_i$, is very great. For ions with average masses τ_{ea} is hundreds of times more than time τ_i; for protons it is 43 times more than τ_i.

Increase of temperature of electrons in compression shock because of transformation of kinetic energy of incident flow of electron gas into heat under the action of forces of electron viscosity is insignificantly small. It is of the order of $\Delta T_e \sim m_e D^2/k$, i.e., m_i/m_e times less than ΔT_i. Heating of electron gas in shock wave occurs by other cause.

Electrons and ions are connected between themselves by electrical forces of interaction. This connection is very strong. The least separation of electron and ion gases leads to the appearance of powerful electrical fields which prevent further separation. Therefore, each particle of plasma remains electrically neutral. Density of electrons n_e always coincides with density of positive charges Zn_i (Z is charge of ions, n_e and n_i are numbers of electrons and ions in 1 cm^3). In the shock wave electron gas behaves not independently, but is compressed exactly as ionic. It is possible to say that electrons are "rigidly attached" to ions by electrical forces. These forces are "external" with respect to electron gas and do not produce dissipation. Inasmuch as dissipation of energy because of the action of forces of electron viscosity is insignificantly small, in compression shock there occurs adiabatic compression and heating of electron gas.

Thus, for instance, during compression of hydrogen plasma by a strong shock wave the density of it is increased in the shock wave four times, in accordance with adiabatic index $\gamma = 5/3$. Temperature of ions can increase very strongly, if amplitude of wave is high, temperature of electrons in shock wave increases only $4^{\gamma-1} = 4^{2/3} = 2.5$ times.

Therefore in a strong shock wave, spreading along plasma with identical temperatures of electrons and ions, after compression shock there appears a sharp distinction in the temperatures of both gases; then in the particle experiencing shock compression there starts the process of transmission of thermal energy from ions to electrons, which leads to temperature balance through a period of the order of the time of exchange τ_{ea} (see § 16, Chapter VI).

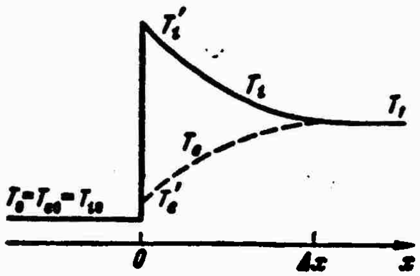

Fig. 7.18. Profiles of ion and electron (dotted line) temperatures in the front of a shock wave in plasma, without taking into account electron thermal conduction.

Width of relaxation zone after compression shock, where there occurs approach to equilibrium state of plasma with equal temperatures $T_e = T_i = T_1$, has an order of $\Delta x \sim u_1 \tau_{ea}$ $(u_1 = \frac{\rho_0}{\rho_1} D)$. Final temperature T_1 is determined by general equations of preservation for front of shock wave. Thus, in the presence of effects connected with the existence of increased electron thermal conduction, distribution of temperatures in the front of the wave should have the form depicted in Fig. 7.18.

If there is no excitation of any other degrees of freedom besides the earlier "frozen" forward degrees of freedom of electrons (as takes place in completely ionized gas), then density of gas and pressure in relaxation zone remain strictly constant. Actually, indices of adiabat of gas with "frozen" and equilibrium degrees of freedom coincide and equal $\gamma = 5/3$, so that compression in shock wave occurs by shock adiabat coinciding with shock adiabat of final state. The physical cause, obviously, consists of the fact that pressure is determined only by average forward energy of particles, which during exchange remains constant and does not depend on distribution of it between particles.

Let us consider now, what influence electron thermal conduction renders on the structure of the front. Till now it has always been considered (and for this there were bases) that dissipative processes, viscosity and thermal conduction, play a role only in the region of large gradients, in a shock wave where macroscopic magnitudes strongly change at distances of the order of a gas kinetic mean free path. In relaxation zone, spreading to distances calculated as many paths, the gradients are small and it is possible to disregard dissipative processes. Really, the characteristic scale serving the criterion of gradient smallness is the scale of length, composed of transport coefficients and speed of front. Transport coefficients, for instance, thermal diffusivity of atoms, are of the order of $\chi \sim l\bar{v}/3$ and scale of length $\lambda \sim \chi/D \sim l\bar{v}/D \sim l$ of the order of gas kinetic mean free path, since thermal velocity of atoms in the front $\bar{v}$ is of the order of speed of front D.

Coefficient of electron thermal diffusivity χ_e is equal approximately to

$$\chi_e = \frac{l_e\bar{v}_e}{3} \sim \frac{l\bar{v}_e}{3}.$$

where l_e is range of electrons, $\bar{v}_e$ is their thermal velocity, and τ_e is time between "collisions" of electrons with each other.

As was shown in § 16, Chapter VI, range of charged particles does not depend on their mass, but depends only on charge and temperature $l \sim T^2/Z^4$.

At comparable temperatures and in light gases, for instance in hydrogen (Z = 1), range of electrons and ions are of electrons and ions are of one order. Speed of electrons is $\sqrt{m_i/m_e}$ times more than speed of ions. Therefore, coefficient of electron thermal conduction is $\sqrt{m_i/m_e}$ times more than coefficient of ionic thermal conduction, and the characteristic scale, on which is performed the process of electron thermal conduction, is

$$\lambda_e \sim \frac{\chi_e}{D} \sim \sqrt{\frac{m_i}{m_e}} \frac{\chi_i}{D} \sim \sqrt{\frac{m_i}{m_e}} l_i.$$

This scale is of the same order as the width of the relaxation zone of temperature balance of electron and ion gases:

$$\Delta x \sim D\tau_{ea} \sim D \sqrt{\frac{m_i}{m_e}} \tau_i \sim \frac{D}{\bar{v}} \sqrt{\frac{m_i}{m_e}} l_i \sim \sqrt{\frac{m_i}{m_e}} l_i.$$

Therefore, with respect to electron thermal conduction, gradients in the relaxation zone are not small and the thermal conduction of heat exchange in this zone will compare with heat exchange between ions and electrons. Electron thermal conduction promotes fastest temperature balance after viscous shock, since it transfers heat, from layers of gas more remote from the compression shock, forward where electron temperature is less. Besides this, and this effect is extraordinarily essential, electron thermal conduction leads to heating of gas before viscous compression shock. Although "hot" ions cannot far escape from behind shock wave into region in front of shock (their thermal velocity is comparable with speed of propagation of shock along undisturbed gas), "hot" electrons with success penetrate forward and outstrip shock wave, since their speed is approximately $\sqrt{m_i/m_e}$ times more than speed of front. Before compression shock will be formed a heated layer. In this layer electron temperature is higher than ionic, since first of all is heated electron gas and only then is heat partially transmitted to ions. In shock wave there occurs a sharp growth of ion temperature. Electron temperature does not change, since its intermittent increase prevents smoothing out because of great thermal conduction. Shock wave has "isoelectronic-thermal" character. Distribution of temperatures in the front of the wave, taking into account electron thermal conduction, is shown in Fig. 7.19.

We will estimate width of heated layer before compression shock. We will consider, for simplicity, that there is no energy transfer from heated electron gas to ionic, and also that gas before compression shock is not compressed and is not retarded (in system of coordinates where front rests). Exact calculations justify these simplifying assumptions. Flow of electron thermal conduction is equal to

$$S = -\varkappa_e \frac{dT_e}{dx} = -\chi_e c_e \frac{dT}{dx}, \qquad (7.33)$$

where $\varkappa_e = \chi_e c_e$ is coefficient of thermal conduction, c_e is heat capacity in 1 cm^3 of electron gas during constant volume.

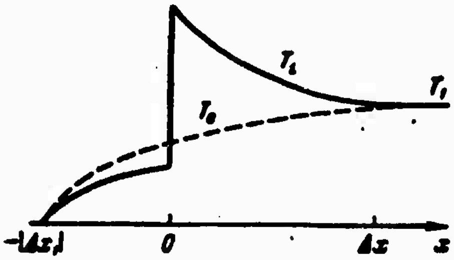

Fig. 7.19. Profiles of ionic and electron (dotted line) temperatures in the front of a shock wave spreading along cold plasma.

Because of stationariness of process flow of thermal conduction in heated layer is equal to hydrodynamic flow of electron energy:*

$$-S = Dc_eT_e = \chi_e c_e \frac{dT}{dx} \qquad (7.34)$$

---

*This is the first integral of equation of energy for given case:

$$c_e \frac{dT_e}{dt} = -\frac{\partial S}{\partial x}; \quad Dc_e \frac{\partial T_e}{\partial x} = -\frac{\partial S}{\partial x}; \quad Dc_eT_e = -S.$$

(initial temperature of electrons before the front is assumed to equal zero; far before wave flow S disappears).

Noticing that $\chi_e \sim \bar{v}_e l_e \sim T_e^{5/2}$ or $\chi_e = aT_e^{5/2}$, where a = const and integrating equation (7.34), we will find

$$x - x_0 = \frac{2}{5}\frac{a}{D}T_e^{-\frac{5}{2}}$$

or

$$T_e = \left[\frac{5}{2}\frac{D}{a}(x - x_0)\right]^{\frac{2}{5}}, \qquad (7.35)$$

where x_0 is coordinate of the front edge of the zone of heating, where temperature turns into zero. Profile of temperature, described by this formula, is depicted schematically in Fig. 7.19. If one were to place origin of coordinates x = 0 at point where shock wave is located, and to designate temperature at this point by T_{e0} (electron temperature on shock does not change), then width of heated layer it is possible to record in the form

$$|x_0| = \frac{2}{5}\frac{a}{D}T_{e0}^{\frac{5}{2}} = \frac{2}{5}\frac{\chi_e(T_{e0})}{D}. \qquad (7.36)$$

During calculation of electron thermal conduction temperature of electrons on shock has the same order as after the front of the wave, so that width of heated layer has the same order as width of relaxation zone after the shock:

$$|x_0| \sim \frac{\chi_e(T_1)}{D} \sim \frac{\bar{v}_e l_e}{D} \sim \sqrt{\frac{m_i}{m_e}}\, l_e \sim \sqrt{\frac{m_i}{m_e}}\, l_i \sim \Delta x_{\text{обмен}}.$$

Width of the heated layer before the compression shock quite rapidly increases with increase in amplitude of wave. If one were to consider that $\chi_e \sim T_e^{5/2} \sim T_1^{5/2}$, and $D \sim T_1^{1/2}$, then from formula (7.36) we will find dependence $|x_0| \sim T_1^2 \sim D^4$.

Obtained profile of temperature is characteristic for nonlinear thermal conduction, when coefficient of thermal conduction decreases with lowering of temperature.* During usual thermal conduction with constant coefficient $\varkappa$ = const, χ = const, we would find from equation of energy that heating exponentially spreads ad infinitum:

$$T = T_1 e^{-\frac{|x|}{x_1}}, \quad T_1 = T(x=0),$$

where characteristic scale $x_1 = \chi/D$. During usual thermal conduction, effective width of zone of heating x_1, in distinction from nonlinear, decreases with growth of amplitude of wave: $x_1 \sim D^{-1} \sim T_1^{-1/2}$.

During calculation of electron thermal conduction in a very strong shock wave, non-ionized gas is strongly heated and is ionized even in front of compression shock so that qualitative characteristics of the structure of a wave spreading along ionized gas remain in force also in the case when a wave spreads along non-ionized gas.

For strict calculation of the structure of the front of a shock wave in completely ionized gas, to general hydrodynamic equations, taking into account flow of electron thermal conduction of the type (7.10), one should add an entropy equation for electron gas, similar to (7.30):

$$\varrho u T_e \frac{d\Sigma_e}{dx} = -\frac{dS}{dx} + \omega_{ea}, \tag{7.37}$$

where ω_{ea} is energy transmitted in 1 cm^3 in 1 sec. from ion gas to electron gas; it is given by formula (7.31).**

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*For greater detail about nonlinear thermal conduction, see Chapter X.

**It is necessary to emphasize that integrals of equations of momentum and energy for a one-dimensional stationary flow of heat-conducting gas (7.10) are accurate only for all gas on the whole. It is impossible to record integrals of equations of momentum and energy for ion and electron gas separately since these equations contain members which are not presented in the form of derivatives with respect to x; for instance, in equations of energy there are members of exchange ω_{ea}. During the composition of equations for both gases members of similar type are reduced, and it is possible to integrate equations for all gas on the whole.

Speeds and compression of both gases at each point are assumed to be identical ($n_e = Zn_1$). Enthalpy and pressure are equal to

$$w = w_i + w_e = \frac{5}{2} AT_i + Z\frac{5}{2} AT_e,$$
$$p = p_i + p_e = A\varrho T_i + ZA\varrho T_e,$$

where A is gas constant calculated per 1 g of plasma.

Entropy of electron gas calculated per 1 g of plasma is equal to

$$\sum\nolimits_e = ZA \ln \frac{T_e^{\frac{3}{2}}}{n_e} + \mathrm{const} = ZA \ln \frac{T_e^{\frac{3}{2}}}{\varrho} + \mathrm{const}. \qquad (7.38)$$

Let us find the condition determining electron temperature in the shock wave.

Let us integrate equation (7.37) by region of shock wave, directing width of it to zero and taking into account the fact that electron temperature at the shock is continuous (it is equal to T_e0). Marking by indices 01 and 02 magnitudes before and after compression shock, we will record result of integration:

$$\varrho_0 DT_{e0} \ln \frac{\varrho_{02}}{\varrho_{01}} = S_{e2} - S_{e1}. \qquad (7.39)$$

Flow at discontinuity experiences a jump; difference of flows on both sides of the discontinuity corresponds to the work of isothermal compression of electron gas by "external" forces effective on the part of the ions.

A system of equations describing the structure of the front it is possible to solve only by means of numerical integration. This was done by V. D. Shafranov [43] for limiting case of a strong wave ($p_1/p_0 \gg 1$) in hydrogen plasma ($Z = 1$) with zero initial temperature. Profiles of temperature and densities are shown in Fig. 7.20. Temperature T_1 here is arbitrary (it is proportional to the square of speed of wave D). For unit of length is accepted magnitude 0.019 $D\tau_{ea_1}$, where τ_{ea_1} is characteristic time of exchange in final state after

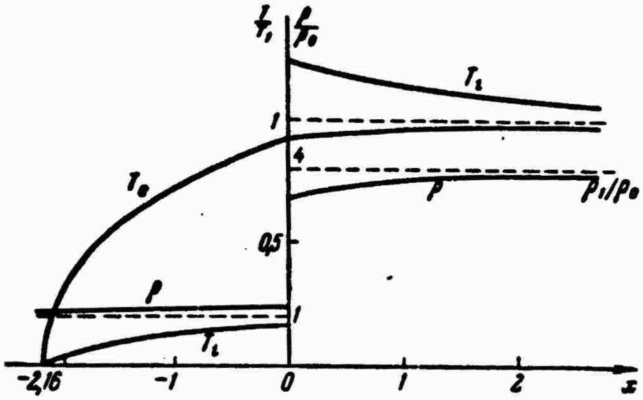

Fig. 7.20. Profiles of temperature and density for a strong shock wave in plasma (figure is taken from work [43]). Electron temperature on shock is equal to $T_e^0 = 0.93\ T_1$; ion temperatures in front of and after shock: $T_{i_1} = 0.16\ T_1$, $T_{i_2} = 1.24\ T_1$. Densities in front of and after shock: $\rho_{01}/\rho_0 = 1.13$, $\rho_{02}/\rho_0 = 3.53$.

front of shock wave; for instance, at initial density $n_i0 = n_e0 = 10^{17}$ cm^{-3} and temperature after fronts $T_1 = 10^{5\,o}$K, $\tau_{ea} = 3.3 \cdot 10^{-9}$ sec. D = 94 km./sec., and unit of length is equal to $5.9 \cdot 10^{-4}$ cm.

§ 13. Polarization of Plasma and Appearance of Electrical Field in a Shock Wave

In preceding paragraph it was assumed that electrons and ions rigidly are connected by electrical forces, and plasma at each point of the shock wave is electrically neutral: density of electrons changes from point to point exactly proportionally to density of ions. In reality this position is not very strictly executed. Thanks to the existence of large gradients of electron density in the compression shock and high mobility of electrons connected with the exceptional smallness of their mass, there are created favorable conditions for the diffusion of electron gas relative to ionic, a change of concentration of electrons, and the appearance of space charges.

Effects of diffusion during propagation of shock wave in a binary mixture of gases were considered in § 5. However, diffusion in plasma, in an essential form, differs from diffusion in a mixture of neutral gases. The fact is that the least change of relative concentration electrons and ions, which leads to the formation of space charges, polarization of plasma, is accompanied by the appearance of a powerful electrical field. This field prevents further polarization and restrains diffusion current of electrons.

Let us estimate, with respect to order of magnitude, how plasma is polarized in the presence of gradients of macroscopic magnitudes, i.e., how far is executed, on the average, the condition of electroneutrality.

For simplicity we will consider hydrogen plasma ($Z = 1$). Let us assume that temperature of electrons is of the order of T, the number of electrons and ions in 1 cm^3 is $n_e = n_i = n$. Let us assume that, further, that there are gradients of macroscopic magnitudes, let us say, density, pressure etc., such that the characteristic dimension of the region in which there occurs noticeable change of magnitudes is of the order of x.

Due to diffusion of electrons in the region of the order of x there is obtained a certain difference in densities of electrons and ions, $\delta n = n_i - n_e$, and there appears space charge $e\delta n$. The appear electrical field $E \sim 4\pi e \cdot \delta n \cdot x$* and potential difference on the boundaries of the region $\delta\varphi \sim Ex \sim 4\pi e\delta n \cdot x^2$. But in the absence of external fields, separation of electrons and ions and potential difference are supported only because of thermal motion of electrons, consequently, potential energy of electrons $e\delta\varphi$ cannot exceed magnitude of the order of kT; $e\delta\varphi \sim 4\pi e^2 \cdot \delta n \cdot x^2 \sim kT$. Hence degree of polarization, i.e., degree of deflection from electroneutrality, in the considered region has an order of

$$\frac{\delta n}{n} \sim \frac{kT}{4\pi e^2 n x^2}.$$

Strong separation of electrons and ions, at which $\delta n/n \sim 1$, can

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*We remind that equation of electrostatics for field strength E and potential φ state:

$$\operatorname{div} E = 4\pi e \cdot \delta n, \quad E = -\operatorname{grad} \varphi.$$

appear only in a thin layer, the thickness of which d is determined by condition $\delta n/n \approx 1 \approx kT/4\pi e^2 nd^2$. Hence

$$d \approx \left(\frac{kT}{4\pi e^2 n}\right)^{\frac{1}{2}} = 6{,}9\left(\frac{T^\circ}{n}\right)^{\frac{1}{2}} \text{ см.}$$

Length d is nothing else but Debye radius (see § 11, Chapter III).* Debye radius characterizes the distance at which plasma shields the electrical field of any charged body, i.e., thickness of so-called double layer forming near the charged body. In particular, a "charged body" can be a separate ion (exactly in this way was introduced the idea of Debye radius in § 11, Chapter III).

By determining d it is possible to record the amount of deviation from electroneutrality in the form $\frac{\delta n}{n} \sim \left(\frac{d}{x}\right)^2$.

The biggest gradients in plasma appear in a viscous shock wave during propagation of a strong shock wave, when macroscopic magnitudes strongly change at a distance of the order of the length of the mean free path of charged particles:

$$l \sim \frac{(kT)^2}{ne^4 \ln \Lambda} \sim 3{,}5\cdot 10^4 \frac{T^{\circ 2}}{n} \text{ см}).^{**}$$

Mean deviation from electroneutrality in the zone of the shock wave is $(x = x_{min} \sim l)$:

$$\frac{\delta n}{n} \sim \left(\frac{d}{l}\right)^2 \sim \frac{e^6 n (\ln \Lambda)^2}{4\pi (kT)^3} \approx 3{,}9\cdot 10^{-8} \frac{n}{T^{\circ 3}}.$$

This magnitude is very small during all reasonable values of densities and temperatures; for instance, at $T = 10^{5\,\circ}$K $n = 10^{18}$ cm^{-3}, $d \approx$ $\approx 0.8\cdot 10^{-6}$ cm, $l \approx 3.5\cdot 10^{-4}$ cm, $\delta n/n \sim 4\cdot 10^{-5}$, $\delta\varphi \sim kT/e = 8.6$ v,*** $E \sim \delta\varphi/l \sim 2.5\cdot 10^4$ v/cm.

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*More exactly, Debye radius multiplied by $\sqrt{2}$, since n in (3.78) is total number of ions and electrons.

**Logarithmic factor in the length of a mean free path (see § 15, Chapter VI) has usually an order of $\ln\Lambda \sim 10$.

***Magnitude $\delta\varphi$ is numerically of the order of temperature, expressed in electron volts.

Let us note that compression of electron gas in a strong compression shock, the width of which is of an order of the length of a mean free path l, occurs only because of electrical forces effective on the part of ions (ion gas is compressed, as usual, because of the action of viscosity). Consequently, potential difference on the shock wave is determined by the work of compression of electron gas going into one electron,

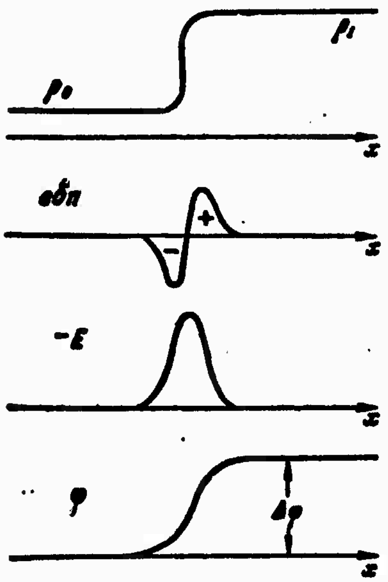

Fig. 7.21. Distributions of mass density, density of space charge, electric field strength, and electrostatic potential in the front of a shock wave spreading along plasma during calculation of diffusion of electrons.

$$e(\varphi_{02}-\varphi_{01}) = kT_{e0}\ln\frac{\varrho_{02}}{\varrho_{01}}.$$

During compression a few times, logarithmic of the order of unity and, consequently, $e\delta\varphi \sim kT$, as was affirmed above.

Distributions of charge, electrical field, and potential in the front of a shock wave in plasma are schematically shown in Fig. 7.21.

The essential difference in distribution of concentrations in a mixture of neutral gases consists of the fact that, along with the region of increased concentration of electrons in the front part of the front of the shock wave, there will appear a region of lowered concentration in the rear part of the wave. In a mixture of neutral gases, in the front of the shock wave there occurs only a concentration of the light component (excess mass of light component flows in from "infinity").

In the case of plasma such a situation is impossible. Concentration of electrons without simultaneous concentration of positive ions in a neighboring region would lead to the appearance of an electrical field to "infinity," i.e., there would be required the expenditure of infinite energy.

In work [45] was considered the structure of the front of a weak shock wave in plasma, taking into account only diffusion of electrons restrained by electrical forces, but without taking into account viscosity and thermal conduction, just as Cowling did [22] for a mixture of electrically neutral gases (see § 5).* As also there, diffusion ensures the blurring of a shock discontinuity of not too great intensity. Thanks to the restraining role of the electrical field, the width of transition layer is smaller than in a mixture of neutral gases.

3. Radiant Heat Exchange in the Front of a Shock Wave

§ 14. Qualitative Picture

When a shock wave spreads along gas occupying a great volume, and the dimensions of the heated region are very great as compared to the mean free path of light, so that temperature of gas little changes at distances of the order of the length of the mean free path, thermal radiation in the volume arrives in local thermodynamic equilibrium with matter. Radiation is equilibrium also directly after the front of the shock wave.

Density of energy and radiation pressure become comparable with density of energy and pressure of matter only during extraordinarily high temperatures or extraordinarily low densities of gas. For instance, in air of normal density this occurs at a temperature of $\approx 2.7 \cdot 10^6$ °K. In shock waves of not so great amplitude radiation pressure and energy are much less than pressure and energy of matter and,

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*See also works [44, 46].

therefore, hardly affect parameters after fronts. Of another order is the relationship of energy flows of radiation and matter, since speed of shock waves with which it is actually necessary to deal is of many orders less than speed of light. The ratio of flows of energy $\sigma T^4/D\rho\varepsilon \sim (U_{rad}/\rho\varepsilon)(c/D)$, roughly speaking, is c/D times more than density ratio of energy. Thus, at $D = 100$ km./sec $c/D = 3\cdot10^3$. In air of normal density, for instance, both flows become identical at a temperature ~300,000°K, at which density of radiation is still very small.

One would think the drain of energy by radiation from the front of a shock wave of great amplitude should play an important role, and in the third of the shock relationships (7.4) it would be necessary, along with the energy flow of the substance to include also flow of energy removed from the surface of the front by radiation $S = \sigma T_1^4$. This would actually affect the final state after the front of the shock wave, leading to large compression after the front, just as an increase in heat capacity of gas leads to large compression. Actually losses of energy to radiation from the surface of the front of the wave are very limited and their effect is usually insignificant. The fact is that in continuous spectrum gases are transparent only for comparatively small quanta. Atoms and molecules strongly absorb quanta, whose energy exceeds ionization potential and which cause photoeffect, and molecules, as a rule, absorb even smaller quanta; for instance, the boundary of transparency of cold air lies at $\lambda \sim 2000\text{Å}$ $h\nu \sim 6$ ev.

At high temperature after the front, energy in the region of small frequencies composes only a small share of the total energy of the spectrum. Thus, at a temperature after fronts of $T = 50{,}000$°K in a region of transparency of air $h\nu < 6$ ev there is concentrated only

4.5% of the energy of plank spectrum. Small quanta are in the Rayleigh — Jeans part of the spectrum and their flow, i.e., possible losses of energy, in any case are proportional not to the fourth, but only to the first degree of temperature.

Radiation from the front of a shock wave, indeed, departs in its basic part to "infinity" only with amplitudes at which the maximum of the plank spectrum lies in the spectral region of transparency of gas, i.e., at temperatures after fronts of the order of 1-2 ev. But with such temperature, absolute value of radiation flux σT_1^4 is minute and additional compression because of losses to radiation in air of normal density does not exceed a percentage.

Thus, the existence of thermal radiation little affects parameters of gas after the front of a shock wave of not too great amplitude. Another matter is the influence of radiation on the internal structure of the transition layer between initial and final thermodynamically equilibrium states of gas, i.e., on the structure of the actual front of the shock wave. Here the role of radiation in waves of large (but presenting real interest) amplitudes turns out to be extraordinarily essential and, moreover, namely radiant heat exchange determines structure of front. The problem concerning the structure of the front of a shock wave, taking into account radiant heat exchange, to which § 14-17 of this chapter are dedicated, was considered by the authors in works [42, 47-49]. Although radiation flux departing from the front of a wave to "infinity" is minute and does not render any power influence on parameters of the shock wave, the fact that it exists has a huge value since it permits observing the wave by optical methods. The question about the glow of a shock wave and the brightness of the surface of the front is tightly interlaced with the question about the structure of the front. It will be considered in Chapter IX.

Due to the nontransparency of cold gas, radiation outgoing from the surface of the shock discontinuity, in waves of great amplitude is almost completely absorbed in front of the discontinuity, heating layers of gas flowing into the discontinuity. This energy, going into heating, is drawn out because of de-excitation of layers of gas, already experiencing shock compression, which, consequently, are cooled by radiation. The effect leads, thus, to transfer of energy from some layers of gas to other means of radiation. Radiation heat exchange is performed at distances measured by the length of the mean free path of quanta for absorption. Usually the length of the mean free path of quanta are several orders larger than the gas kinetic mean free path of particles (see Chapter V) and larger than the width of the relaxation layer, where thermodynamic equilibrium is established in the actual substance.

Thus, in air of normal density lengths of the mean free paths of quanta with energies of $h\nu \sim$ 10-100 ev, corresponding to temperatures after the front of $T_1 \sim 10^4 - 10^5$ °K, have an order of $10^{-2} - 10^{-1}$ cm, whereas a gas kinetic path is of the order of 10^{-5} cm.

Width of the front of a shock wave in which radiant heat exchange plays an essential power role is determined by the length of the mean free path of light — the largest scale of length. With some meaning it is possible to speak about relaxation of radiation in the front of a shock wave and about the establishment of equilibrium of radiation with the substance after the front.

Let us trace qualitatively, how the structure of the front changes during transition from waves of small amplitude to waves of great amplitude. With this we will consider the phenomenon in "large scale," not being interested in "small scale" component connected with relaxation in different degrees of freedom of gas, i.e., assuming that at each point of the wave the substance is in a state of thermodynamic equilibrium. A viscous shock wave together with the relaxation zone after it we will consider as a mathematical discontinuity.

In the limiting case of a sufficiently weak wave, when the power role of radiation is small, profiles of all magnitudes in the shock wave have the character of the "classical" steps (Fig. 7.22). During growth of amplitude rapidly grows flow of radiation from the surface of the front — σT_1^4. Radiation is absorbed before the discontinuity at a distance of the order of the mean free path of quanta and heats the gas; heating is less the further from the discontinuity due to absorption of radiation flux. The shock wave is propagated now not along the cold but along the heated gas and temperature after the shock T_+ is higher than in the absence of heating, i.e., higher than in the final state. After the compression shock temperature decreases from T_+ to T_1. In other words, a particle of gas flowing through the shock wave at first is heated by radiation, but after experiencing shock compression it is cooled, de-exciting part of the energy which goes into creation of radiation flux. Heating of gas before the discontinuity leads to increase of its pressure and a certain compression (and also to braking in the system of coordinates where the front rests). In the shock wave gas is compressed to a density somewhat smaller than final. Cooling of gas after the compression shock promotes its further compression to final density (as also in the case of lowering temperature due to excitation of additiona

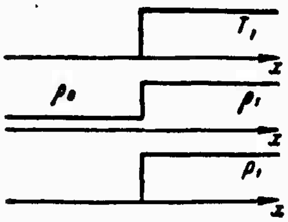

Fig. 7.22. Profiles of temperature, density, and pressure in a "classical" shock wave.

degree of freedom). Pressure increases.

Profiles of temperature, density, and pressure in the wave, responding to the described picture, are depicted schematically in Fig. 7.23.

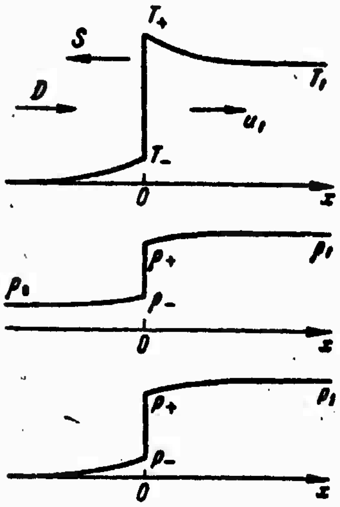

Fig. 7.23. Profiles of temperature, density, and pressure in the front of a shock wave of not too great amplitude during calculation of radiant heat exchange.

Temperature of heating before discontinuity T_- is proportional to radiation flux outgoing from the surface of discontinuity — $S_0 \approx \sigma T_1^4$, and is quickly increased with growth of amplitude of wave. Thus, in air of normal density $T_- \approx 1400^\circ K$ at $T_1 = 25{,}000^\circ K$; $T_- = 4000^\circ K$ at $T_1 = 50{,}000^\circ K$; $T_- = 60{,}000^\circ K$ at $T_1 = 150{,}000^\circ K$. Correspondingly is increased excess of temperature after shock T_+ over final T_1 (roughly speaking, $T_+ - T_1 \approx T_-$).

At a certain temperature after the front $T_1 = T_{crit}$ temperature of heating T_- attains magnitude T_1 and profile of temperature obtains the form shown in Fig. 7.24. This temperature T_{crit}, equal approximately to $300{,}000^\circ K$ for air, can be called critical since it divides two essentially different cases of structure of the front of the shock wave.

Let us consider a wave of great, supercritical amplitude with temperature after the front $T_1 > T_{crit}$. Energy flow of quanta radiated by gas after the compression shock and outgoing from the surface of discontinuity in the direction of cold gas would suffice to heat a layer of the order of the length of a mean free path in which quantum is absorbed, up to a very high temperature, of more than T_1. Can heating in fact be carried out so high? Obviously not, since the heated layer itself would begin intensely to radiate and is rapidly cool to temperature T_1. Appearance of state with $T_- > T_1$ would signify that in a closed system heat is inadvertently transferred from less heated layers of gas to more heated, in contradiction of the second law of thermodynamics.* In fact, energy removed by radiation from gas heated in a shock wave is simply expended on heating thicker layers before the discontinuity. Quanta going out from behind the surface of discontinuity are absorbed in front of the discontinuity in a layer of the order of the length of the mean free path and heated to a temperature close to T_1; the substance itself radiates, heating neighboring layers, etc. We will deal with a typical case of the heating of gas by means of radiant thermal conduction. Before the discontinuity spreads a thermal conduction wave, gripping a thicker layer of gas the larger the amplitude of the shock wave. The phenomenon is fully analogous to a shock wave with electron thermal conduction, which was conduction, which was considered in § 12 (radiant thermal conduction also in nonlinear).

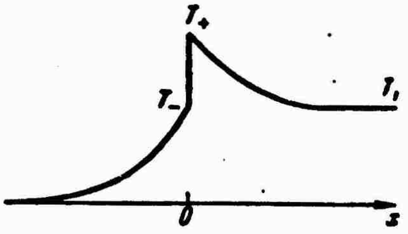

Fig. 7.24. Profile of temperature in a shock wave of "critical" amplitude.

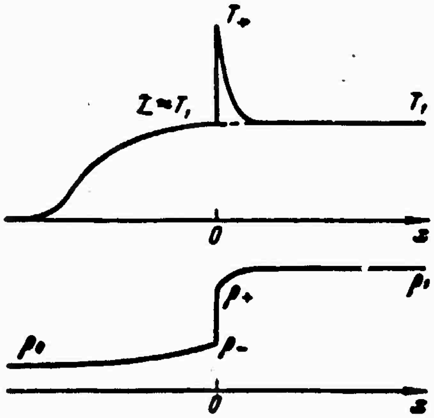

Fig. 7.25. Profiles of temperature and density in the front of a shock wave of very great amplitude during the calculation of radiant heat exchange. Dotted line corresponds to approximation of radiant thermal conduction (isothermal jump).

Profiles of temperature and density in a shock wave of supercritical amplitude are depicted in Fig. 7.25. After compression shock, as before, there is a peak of

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*In greater detail, the impossibility of a state with $T_- > T_1$ will be discussed in § 17. Strict proof of this position is given in work [42].

temperature, appearing as a result of shock compression. As also earlier, particles of gas, after experiencing shock compression, are cooled, de-exciting part of their energy, and they return it to creation of thermal wave before the discontinuity.

However, in distinction from a subcritical case, thickness of the peak is now less than the mean free path of radiation and decreases with growth in amplitude of wave (see § 17).

In approximation of radiant heat exchange, when from consideration are dropped parts of phenomena occurring at distances less than the mean free path, the peak will be "cutoff," as was shown by dotted line in Fig. 7.25, and shock wave obtains the character of an "isothermal" shock (see § 3 this chapter).

In subsequent paragraphs the physical picture outlined here in broad terms will be given a mathematical basis.

§ 15. Approximate Formulation of the Problem About Structure of a Front

We will consider, as usual, a one-dimensional steady-state operation in system of coordinates where the front rests. For clarification of peculiarities of structure of front, connected with radiant heat exchange, we will introduce a number of simplification. The gas we will consider ideal, possessing constant heat capacity, so that its pressure and specific internal energy are expressed by simple formulas:

$$p = A\varrho T, \quad \varepsilon = \frac{1}{\gamma - 1} AT.$$

Viscous compression shock, together with relaxation layer where there occurs establishment of thermodynamic equilibrium in the substance, we will replace by a mathematical discontinuity. In the zone of radiant heat exchange we will disregard relaxation phenomena, viscosity and thermal conduction of the substance, and also electron thermal conduction.* The shock wave we will consider strong (initia pressure and energy of the substance are small as compared to final) We will not consider waves of extraordinarily great amplitude; in this case it is possible to disregard energy and pressure (but not flow!) of radiation.

Small flow of small quanta, departing from the front of the wav to "infinity," we do not take into account, considering that before the front radiation flux is equal to zero.

With the assumptions made the system of integrals of equations of hydrodynamics (7.10) takes the following form:

$$\left.\begin{aligned} \rho u &= \rho_0 D, \\ p + \rho u^2 &= \rho_0 D^2, \\ \varepsilon + \frac{p}{\rho} + \frac{u^2}{2} + \frac{S}{\rho_0 D} &= \frac{D^2}{2}. \end{aligned}\right| \tag{7.40}$$

Here S is energy flow of radiation. Let us note that it is directed toward flow of gas, which moves to positive side of axis x, so that $S < 0$ $(D, u > 0)$.

Before the fronts at $x = -\infty$, and after the front of the shock wave, at $x = +\infty$, flow is $S = 0$, and all quantities take their initi and final values with which, as always we will add indices "0" and "1." Coordinate x we will count off from point where shock wave is located.

For determination of radiation flux, it is necessary to join equation of radiation transfer to equations of hydrodynamics (7.40). We will consider angular distribution of quanta in diffusion approximation, replacing strict kinetic e[illegible]ion for intensity by two equations for density and radiation flux (see § 10, Chapter II).

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*Appraisals show that in a number of real cases, including such a practically important process, as shock wave in air of normal normal density, electron thermal conduction plays a smaller role than transfer of energy by radiation (see [48]).

Let us emphasize that in the diffusion approximation there are formally contained no assumptions about the nearness of radiation density to equilibrium and the diffusion approximation is by no means equivalent to the approximation of radiant thermal conduction. With its help we describe also essentially nonequilibrium radiation, only by approximate form while considering angular distribution of quanta (see § 13, Chapter II).

We will operate with only integral values of density and flux of radiation U and S over the spectrum, for which we will introduce a certain average length of mean free path of light l over the spectrum. As was marked in Chapter II, such an approximation, strictly speaking, is possible only in defined limiting cases. However, it does not distort qualitative regularities of radiant transfer and for our purpose is sufficient.

Let us copy equations for radiation in shown approximations (see formulas (2.62) and (2.65)):

$$\frac{dS}{dx}=\frac{c(U_p-U)}{l},$$

$$S=-\frac{lc}{3}\frac{dU}{dx}.$$

Here $U_p = 4\sigma T^4/c$ is density of energy of equilibrium radiation, corresponding to temperature of the substance at a given point x.

Equation of hydrodynamics and transfer of radiation do not contain in evident form coordinate x; therefore, in them it is possible to cross to new coordinate — optical thickness τ, which is counted off from point x = 0 in positive direction of axis x:

$$d\tau=\frac{dx}{l},\quad \tau=\int_0^x\frac{dx}{l}. \qquad (7.41)$$

If length of mean free path l is known as a function of temperature and density of gas, in the final solution it is easy with the help of equations (7.41) to cross from distributions of different magnitudes with respect to optical coordinate to distributions with respect to x (at l = const both types of profiles, obviously, coincide). In terms of optical thickness, equations of transfer obtain such form:

$$\frac{dS}{d\tau}=c(U_p-U), \tag{7.42}$$

$$S=-\frac{c}{3}\frac{dU}{d\tau}. \tag{7.43}$$

Equations of hydrodynamics (7.40) and transfer of radiation (7. (7.43) together with natural boundary conditions, expressing the absence of radiation in cold gas before the wave and the thermodynamically equilibrium character of the radiation after the front of the wave,*

$$\tau=-\infty,\ S=0,\ U=0,\ T=0, \tag{7.44}$$

$$\tau=+\infty,\ S=0,\ U=U_{p_1}=\frac{4\sigma T_1^4}{c},\ T=T_1, \tag{7.45}$$

completely describe the structure of the front of a shock wave in the presented setting. The system of differential equations has second order. It is possible to lower the order if one excludes from the system coordinate τ, dividing equation (7.42) and (7.43) one by the other:

$$\frac{dS}{dU}=\frac{c^2}{3}\frac{U-U_p}{S}. \tag{7.46}$$

For explanation of the physical meaning of laws of structure of the front diagrams p, V; T, V; S, V, considered in § 3, are very convenient. Introducing, as there, relative specific volume $\eta = V/V_0$ equal to reciprocal of compression and dimensionless speed

$$\eta=\frac{V}{V_0}=\frac{\rho_0}{\rho}=\frac{u}{D},$$

we will find from the first two equations of (7.40) that in regions where gas dynamic magnitudes are continuous, pressure changes along

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*From these conditions only two are independent; the others are results of equations.

straight line

$$p = \rho_0 D^2 (1 - \eta). \tag{7.47}$$

Temperature and flow depend on compression by formulas, analogous to (7.13) and (7.14). These formulas are obtained from equations (7.40) in the case of gas with constant heat capacity. Let us introduce in formulas (7.13) and (7.14), instead of Mach number, temperature after the front of the shock wave T_1. We will obtain

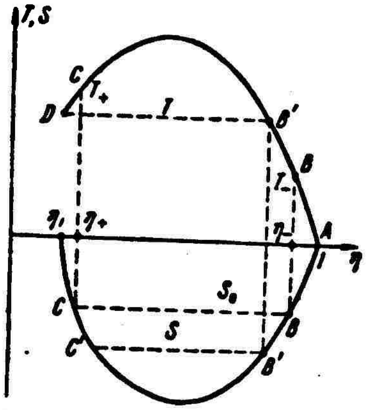

Fig. 7.26. T, η and S, η-diagrams for a shock wave, taking into account radiant heat exchange.

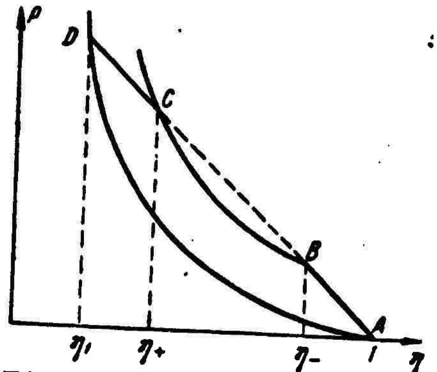

Fig. 7.27. p, η-diagram for a shock wave, taking into account radiant heat exchange.

$$T = \frac{T_1 \eta (1 - \eta)}{\eta_1 (1 - \eta_1)}, \tag{7.48}$$

$$S = -\frac{\rho_0 D A T_1 (1 - \eta)(\eta - \eta_1)}{2\eta_1^2 (1 - \eta_1)}, \tag{7.49}$$

where $\eta_1 = (\gamma - 1)/(\gamma + 1)$. Radiation in a shock wave plays an essential role only at high temperatures, when gas is strongly ionized. The effective adiabatic index in region of ionization, for numerical appraisals, it is possible to assume as equal to $\gamma = 1.25$. Corresponding compression after front of wave $1/\eta_1 = 9$, $\eta_1 = 0.111$.

Function $T(\eta)$, $S(\eta)$, $p(\eta)$ are depicted in Fig. 7.26 and 7.27. Curve $T(S)$, which can be obtained from equations (7.48), (7.49), as may be seen from Fig. 7.26, has two branches: one of them, which in limit $S \to 0$ gives $T \to 0$ ($\eta \to 1$), corresponds to states close to initial, i.e., zone of heating before discontinuity; the other, with limit $S \to 0$, $T \to T_1$, $(\eta \to \eta_1)$, corresponds to states close to final, i.e., region after discontinuity.

In the subsequent two paragraphs we will find approximate solutions of equations of regime for the two extreme cases described in § 14: for shock waves of subcritical and supercritical amplitudes. It is necessary to note that transition from one case to another is continuous. Simply for intermediate values of amplitudes close to critical, it is not possible to find solution in an analytic form. Numerical integration for intermediate amplitudes is no difficulty. However, there is no particular necessity for it since the found, limiting, analytical solutions are valid up to amplitudes very close to critical from any direction.

§ 16. Shock Wave of Subcritical Amplitude

Let us consider a shock wave of small amplitude, in which all effects connected with radiation, are great. Temperature after compression shock is close to final temperature and from surface of discontinuity emerges radiation flux equal in absolute value to $|S_0| \approx \approx \sigma T_1^4$. Let us trace state of particle of gas, flowing into wave. Current point on diagrams T, η; S, η; p, η moves from initial position A in the direction of compression up to position B, in which flow is equal to S_0. Density of gas, temperature, pressure, and radiation flux in the particle monotonically grow during approach to discontinuity. From formulas (7.48) and (7.49) it follows, and this one may see from Fig. 7.26, that on those branches of curves, which emerge from initial point A, i.e., in the zone of heating, compression is very small. Even at $T = T_1$ on this branch compression composes only $1/(1 - \eta_1) = 1.13$ (if $\gamma = 1.25$, $\eta_1 = 0.111$), and during temperatures before discontinuity T_- smaller than T_1, compression in the heating zone is still less. If one were to approximately exclude η from equations (7.48) and (7.49) and express S through T with an accuracy up to small terms of the second order relative to η_1, we will obtain

$$-S=\frac{D\rho_0\Delta T}{\gamma-1}=D\rho_0\varepsilon. \tag{7.50}$$

This equation, which is obtained from integral of energy (7.40), if one were to omit in it members p/ρ, $D^2/2$, $u^2/2$, has a simple physical meaning. It means that energy of absorbed radiation in zone of heating is expended only on increase of temperature of gas. And indeed, it is easy to show that work of compression p/ρ and change of kinetic energy $(D^2/2) - (u^2/2)$, which basically are proportional to η_1 with an accuracy of small terms of the second order, proportional to η_1^2, compensate one another.

Equation of energy conservation in the absence of braking and compression of gas, recorded in the form

$$-S=D\rho_0\varepsilon(T,\rho_0) \tag{7.51}$$

is valid even in the general case when heat capacity depends on temperature. If one were to carry it to point x = 0 directly before discontinuity, we will find maximum temperature of heating T_-:

$$|S_0|\approx\sigma T_1^4=D\rho_0\varepsilon(T_-). \tag{7.52}$$

In gas with constant heat capacity $D\sim\sqrt{T_1}$ and $T_-\sim T_1^{3,5}$, i.e., heating rapidly grows with growth of amplitude of wave. By equation (7.52) it is possible approximately to estimate that temperature after the front, at which temperature before compression shock T_- attains magnitude T_1 (we called such a wave critical). The approximation consists in the fact that flow from the surface of discontinuity, as before, is assumed equal to σT_1^4, whereas in reality it is somewhat more since temperature after discontinuity is somewhat higher than T_1. Approximate equation for determination of critical amplitude $T_1 = T_{crit}$ is

$$\sigma T_{\text{кр}}^4 = D(T_{\text{кр}})\rho_0 \varepsilon(T_{\text{кр}}). \tag{7.53}$$

Table 7.2

$D, \frac{\text{км}}{\text{sec}}$	T_1, °K	$\varepsilon_-, \frac{\text{eV}}{\text{molecule}}$	T_-, °K	$D, \frac{\text{км}}{\text{sec}}$	T_1, °K	$\varepsilon_-, \frac{\text{eV}}{\text{molecule}}$	T_-, °K
23,3	50 000	3,7	4 000	56,5	150 000	122	60 000
28,5	65 000	8,4	9 000	81,6	250 000	635	175 000
32,1	75 000	13,1	12 000	86,2	275 000	910	240 000
40,6	100 000	32,7	25 000	88,1	285 000	1020	285 000

In Table 7.2 are given (calculated by formula (7.52) values of temperature before compression shock in air of normal density when considering real dependence $\varepsilon(T)$. From the table it is clear that critical temperature in air is equal to approximately 300,000°K (285,000°K according to equation (7.53)). As follows from determination (7.53), critical temperature is the temperature at which energy flows of matter and radiation become approximately identical (we will remember remark in the beginning of § 14).

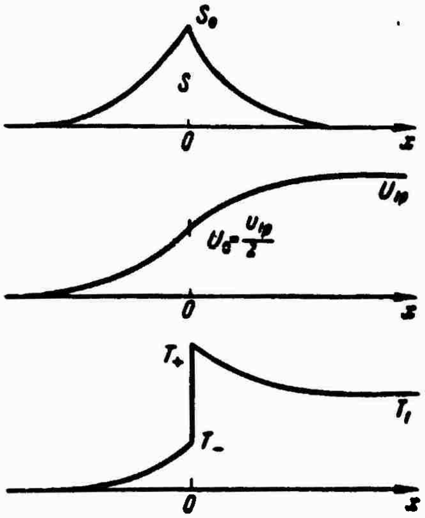

Fig. 7.28. Profiles of flow and density of radiation and temperature in a shock wave of subcritical amplitude.

Returning to initial equations for gas with constant heat capacity, we will find approximate solution in the zone of heating of a subcritical wave. If temperature in the zone of heating is low as compared to temperature after the front ($T_- < T_1$), then equilibrium density of radiation, proportional to fourth degree of temperature of gas ($U_p \sim T^4$), is much less than actual density U, which is determined by radiation penetrating the gas coming from behind the surface of discontinuity and having temperature T_1 ($U \sim |S_0| \sim T_1^4$).

Radiation generated in the actual zone of heating gives small contribution to total flux and density. Density of radiation, thus, is essentially nonequilibrium in the zone of heating. Disregarding in equations (7.42) and (7.46) U_p as compared to U, we will find solution before the discontinuity during $\tau < 0$:

$$-S = \frac{cU}{\sqrt{3}} = -S_0 e^{-\sqrt{3}|\tau|}, \tag{7.54}$$

$$T = T_- e^{-\sqrt{3}|\tau|}, \tag{7.55}$$

$$\frac{\rho - \rho_0}{\rho_0} = \frac{\rho_- - \rho_0}{\rho_0} e^{-\sqrt{3}|\tau|}, \tag{7.56}$$

$$p = p_- e^{-\sqrt{3}|\tau|}. \tag{7.57}$$

All magnitudes exponentially drop in optical thickness according to their distance from the discontinuity (Fig. 7.28). Values T_-, ρ_-, p_- are easy to calculate with the help of formulas (7.52) and (7.48) and equations of state.

At point of shock discontinuity, density and radiation flux remain continuous. Really, discontinuity in density of radiation would correspond, by the formula (7.43), to infinite flow, which in reality is limited by laws of conservation of energy, and discontinuity in flow would lead to non-stationary accumulation or decrease of energy of radiation at point of discontinuity. Consequently, current point on diagrams T, η; S, η during passage of viscous shock jumps from position B on one branch of curves to other branch at position C, corresponding to the very same flow S_0. (Derivative of flow, of course, endures a discontinuity). The same occurs also with point on diagram p, η: gas is compressed in shock wave in accordance with shock adiabat CB passing through point B. After shock compression, state of particle monotonically nears final, toward point D. Temperature and radiation flux decrease, and density of gas and pressure increase.

In a wave of low amplitude, the excess of temperature after discontinuity T_+ above temperature after front T_1, as can be seen from diagram T, η, just as the change of volume after discontinuity, is small. Excluding, as earlier, η from equations (7.48) and (7.49), for the second branch we will find, with an accuracy up to small terms of the second order relative to η_1, connection of flow and temperature after discontinuity:

$$-S = \frac{3-\gamma}{\eta_1} D\varrho_0 A (T - T_1). \tag{7.58}$$

In order to decide approximately equation of radiation transfer in the region after the discontinuity, we note that temperature here changes and it is possible to assume $U_p \approx U_{p1} = 4\sigma T_1^4/c = \text{const}$. Let us obtain at $\tau > 0$:

$$-S = \frac{c}{\sqrt{3}} (U_{p1} - U) = -S_0 e^{-\sqrt{3}\tau}, \tag{7.59}$$

$$T - T_1 = (T_+ - T_1) e^{-\sqrt{3}\tau}, \tag{7.60}$$

where $T_+ - T_1 = [(3 - \gamma)/(\gamma + 1)]\, T_- \approx 0{,}78\, T_-$ at $\gamma = 1.25$.

Value of radiation density at point of discontinuity we will find, joining at point $\tau = 0$ two branches of curves U(S), which are given by formulas (7.54) and (7.59). Let us obtain*

$$U_0 = \frac{1}{2} U_{p1} = 2\sigma T_1^4. \tag{7.61}$$

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*Let us note that with this there appears a new value of flow $S_0 = (2/\sqrt{3})\sigma T_1^4$, somewhat differing from former: $S_0 = \sigma T_1^4$. This small disharmony is a consequence of the imperfection of diffusion approximation and disappears during use of exact equation of radiation transfer; see about this in work [47].

Profiles of density and radiation flux in subcritical wave are depicted in Fig. 7.28, where for comparison is given also profile of temperature.

Let us look at the limits of applicability of approximate solution of equations in zone of heating. Formula (7.50) has high accuracy even in a wave of critical amplitude, since at $\gamma = 1.25$ compression before discontinuity is small: $\rho_{-}/\rho_0 << 1.13$.

Regarding, however, solution of radiation transfer equation (7.54), it is obtained in approximation $U_p << U$ and loses force when density of radiation U becomes comparative with equilibrium. From formulas (7.54) and (7.50) it follows, that this occurs at temperature T_K, satisfying equation

$$\frac{4\sigma T_K^4}{\sqrt{3}} = \frac{D\rho_0 A T_K}{\gamma - 1}, \tag{7.62}$$

Comparing this equation with expression (7.53), in which we consider heat capacity constant $\left(\varepsilon = \frac{1}{\gamma - 1} AT\right)$ and noticing that D weakly depends on temperature ($D \sim \sqrt{T_1}$ at γ = const), we see that temperature T_K is very close to critical temperature T_{crit}. It follows from this that density of radiation in heating zone always is nonequilibrium temperatures lower than critical and our approximate solution is valid for waves with amplitudes up to critical.

It is essential that radiation density becomes of the order of of equilibrium, when are energy flows of radiation and hydrodynamics are equal. As can be seen from formulas (7.54)-(7.57), optical thickness of zone of heating in a wave of subcritical amplitude has the order of unity. Geometric width of zone, consequently, is of the order of the average mean free path of radiation over the spectrum. In air of normal density this width is of the order of 10^{-2} - 10^{-1} cm.

The bigger it is the higher the temperature behind the front since the mean free path grows with increase of energy of quanta. The same order approximately has the width of the zone after compression shock, where there occurs approach to final states of gas and radiation.

§ 17. Shock Wave of Supercritical Amplitude

Let us consider a shock wave of great, supercritical amplitude, when temperature after front $T_1 > T_{crit}$. Temperature in the zone of heating increases from zero to magnitude T_-, which is equal to final T_1 and, consequently, also largely than T_{crit}. Inasmuch as temperature T_K, defined by formula (7.62), is close to critical T_{crit}, T_- is larger than T_K. Compression in the zone of heating is small and equation (7.50) remains in force.

On the front edge of the zone where temperature is lower than magnitude T_K, radiation as before is nonequilibrium and solution of the type (7.54), (7.55) is valid, in which T, S and U exponentially drop with optical thickness. At the point where temperature attains magnitude T_K, density of radiation becomes of the order of equilibrium and flow S of the order of Stefan — Boltzmann flow σT^4. During further advance in the direction toward discontinuity, radiation flux grows owing to law of preservation (7.50) proportionally to the temperature ($S \sim T$), i.e., becomes less than Stefan — Boltzmann flow σT^4. This means that in temperature region where $T > T_K$, one-sided flows of opposite direction (which are of the order of σT^4) to a considerable degree compensate one another; generation of radiation at every point is comparable with absorption and, consequently, density of radiation is close to thermodynamic equilibrium. In other words, in the shown region of the zone of heating radiation is in local equilibrium with substance, and radiation transfer has the character of radiant thermal conduction. Flow S is now determined by gradient of temperature, and the smallness of it as compared to Stefan — Boltzmann corresponds to the fact that temperature little changes at a distance of the order of the mean free path of light. In order to obtain solution in the zone of radiant thermal conduction, one should replace, in equation of diffusion (7.43), density of radiation U equilibrium magnitude $U_p \approx U$:

$$S = -\frac{c}{3}\frac{dU_p}{d\tau} = -\frac{16\sigma cT^3}{3}\frac{dT}{d\tau}. \qquad (7.63)$$

Solving this equation jointly with algebraic equation (7.50), we will find profiles of temperature, flow, and density of radiation in the equilibrium region of the zone of heating. They have to be joined with the solution on the front edge in the nonequilibrium region at a point with temperature $T = T_K$, effectively differentiating both regions. Optical coordinate of this point we will designate by τ_K. After elementary calculation we will obtain solution in nonequilibrium region, at $\tau < \tau_K$, $|\tau| > |\tau_K|$,

$$\frac{T}{T_K} = \frac{cU}{4\sigma T_K^4} = \frac{\sqrt{3}\,S}{4\sigma T_K^4} = e^{-\sqrt{3}|\tau-\tau_K|}; \qquad (7.64)$$

in equilibrium region, at $\tau_K < \tau < 0$, $0 < |\tau| < |\tau_K|$,

$$\frac{T}{T_K} = \frac{\sqrt{3}S}{4\sigma T_K^4} = \left(\frac{cU}{4\sigma T_K^4}\right)^{\frac{1}{4}} = \left(1 + \frac{3\sqrt{3}}{4}|\tau-\tau_K|\right)^{\frac{1}{3}}, \qquad (7.65)$$

where τ_K is expressed through temperature before discontinuity

$$|\tau_K| = \frac{4}{3\sqrt{3}}\left[\left(\frac{T_-}{T_K}\right)^3 - 1\right]. \qquad (7.66)$$

Inasmuch as temperature in nonequilibrium zone drops exponentially, while decreasing a few times at optical distance equal to unity, magnitude $|\tau_K|$ in the case of a very strong wave, when $T_-^3 \gg T_K^3$, constitutes the optical thickness of the zone of heating.

It is necessary to note that in the equilibrium region mean free path light is averaged by Rosseland (see § 12, Chapter II). Temperature before the discontinuity in supercritical wave T_- almost coincides with temperature after front T_1.

Temperature before discontinuity T_- never can become higher than final temperature after front T_1. Really, if $T_- > T_1$, then density of radiation in the zone of heating before the discontinuity, which is equal to approximately $U_- \approx \frac{4\sigma T_-^4}{c}$, becomes larger than density of radiation after the front $U_{p1} = \frac{4\sigma T_-^4}{c}$. Consequently, in the zone between discontinuity and region of final state $(0 < \tau < +\infty)$ density of radiation decreases as distance from discontinuity increases. Flow, which is proportional to $S \sim -\frac{dU}{d\tau}$, is positive and is directed in the direction of the motion of gas. But this contradicts formulas (7.48) and (7.49), which are a consequence of the laws of preservation and which indicate that flow in a shock wave everywhere is negative and is directed opposite to the motion of gas.

Thus, temperature T_- is limited from above by magnitude T_1.

The fundamental impossibility of heating gas before the compression shock to a temperature exceeding the temperature after the front T_1, simultaneously attests to the necessity of the appearance of discontinuity in solution (current point on diagrams T, η; S, η, so that to reach final position D, it must "jump" from position B' to another branch of the curves). The presented physical considerations about the impossibility of an excess of temperature T_- above T_1 and the necessity of the appearance of a discontinuity find their confirmation in the strict investigation of equations of regime (see work [42]).

Inasmuch as in supercritical wave $T_- \approx T_1$ and density of radiation before discontinuity is close to equilibrium, it still before discontinuity almost attains its final volume. Thus,

$$U_0 = U_- \approx \frac{4\sigma T_-^4}{c} \approx \frac{4\sigma T_1^4}{c} = U_{p1}, \tag{7.67}$$

and in the region after discontinuity density of radiation remains practically constant:

$$U(\tau) \approx U_{p1} = \frac{4\sigma T_1^4}{c} \quad \text{at} \quad \tau > 0. \tag{7.68}$$

From formula (7.65) it follows that flow at point of discontinuity is equal to

$$S_0 = \frac{4\sigma T_{\text{к}}^4}{\sqrt{3}} \frac{T_1}{T_{\text{к}}}. \tag{7.69}$$

On diagrams T, η; S, η, current point in supercritical wave moves along curves from point A to point B', and then skips point C', where flow is the same. Temperature after discontinuity T_+ it is possible to calculate by the formulas (7.48) and (7.49). It is equal to

$$T_+ = (3-\gamma) T_1. \tag{7.70}$$

If one were to use approximation of thermal conduction in the region after the discontinuity, then, in accordance with obtained condition of constancy of radiation density in this region, temperature of gas also turns out to be constant. Temperature on the shock wave is continuous and is equal to final T_1. Current point on diagrams T, η; S, η from position B' immediately before the discontinuity moves straight to final position D. The flow, of course, experiences discontinuity since before the compression shock it is different than zero and is equal to S_0, and in final state (point D) it is equal to zero.

Thus, we are dealing with a typical case of "isothermal jump," which we have already encountered in § 3 and 12.

Appearance of "isothermal jump" is a consequence of mathematical approximation, in which flow is considered proportional to gradient of temperature. This excludes the possibility of the existence of a temperature jump, since during discontinuity of temperature flow becomes infinite.

Actually, because of the stationariness of the process in the shock wave, flow is continuous, but temperature experiences a discontinuity.

There are no contradictions here: simply in the region after discontinuity radiation is nonequilibrium (density is lower than equilibrium since density corresponds to temperature $T_- \approx T_1$, and temperature of gas $T_+ > T_1$) and flow, which is determined by gradient of true density of radiation, is not expressed through gradient of temperatures. After shock discontinuity, as before, there is a peak of temperature, and the profile of temperature in the supercritical wave has the form depicted in Fig. 7.25.

We will estimate optical thickness of the peak of temperature after discontinuity on simple physical considerations. Geometric thickness of peak Δx is such that radiation born in this zone gives flow S_0, outgoing from surface of discontinuity and going into the heating of gas flowing in wave. Energy radiated in 1 sec. in layer Δx (per 1 cm^2 of surface of discontinuity), is of the order of

$$\frac{\sigma T_+^4}{l}\Delta x \sim \frac{\sigma T_K^4}{l}\Delta x.$$

This magnitude approximately is equal to flow S_0, which, according to formula (7.69), is of the order of $S_0 \sim \sigma T_K^3 T_1$. Hence is obtained thickness of peak of temperature:

$$\Delta\tau = \frac{\Delta x}{l} \sim \left(\frac{T_K}{T_1}\right)^3. \qquad (7.71)$$

It fast decreases with increase of amplitude of wave, and in a very strong wave peak is much thinner than mean free path of radiation. Therefore, it also will be "cut" in the approximation of radiant thermal conduction, from which will fall out parts connected with distances smaller than the mean free path of radiation.

In conclusion we will give the value of the width of the zone of heating in a shock wave of supercritical amplitude spreading along air of normal density. These values are estimated with the help of formula (7.66) and calculated by the method in § 8, Chapter V of Rosseland mean free paths of radiation in real air. At $T_1 = 500{,}000^\circ K$, $\tau_k = 3.4$, and width is of the order of 40 cm. At $T_1 = 750{,}000^\circ K$ $\tau_k = 14$, and width is of the order of 2 m. Inasmuch as peak of temperature is very narrow, these widths at the same time represent also the width of all the front of the shock wave.

§ 18. Shock Wave During Large Density of Energy and Radiation Pressure

In § 3 it was shown that in a shock wave not too weak, in a case when there is thermal conduction but no viscosity, continuous transition of gas from initial state to final is impossible. Discontinuity unavoidably appears, which corresponds to viscous shock wave, and in the framework of the given approximation it is infinitely thin (since from the very beginning the viscosity of matter was excluded from consideration). If thermal conduction flow is proportional to gradient of temperature, then on discontinuity all magnitudes experience a jump, with the exception of temperature: an "isothermal" jump takes place. In § 12 and 17 were examined concrete examples of "isothermal" jumps, to which electron and radiant thermal conductions lead.

However, at extraordinarily large amplitudes of shock wave, when density of energy and radiation pressure become sufficiently large as compared to energy and pressure of the substance, the position changes. Discontinuity disappears and gas in the shock wave passes continuously from initial state to final only because of radiant thermal conduction, even if viscosity of the substance is not taken into account. This question was considered by S. Z. Belen'kiy and (later) by B. A. Belokon' [50].

For description of the internal structure of the front of the shock wave, we will originate from general hydrodynamic equations (7.40) where S is flow of radiant thermal conduction. Total pressure and energy are composed of magnitudes pertaining to substance and radiation, where radiation is considered in thermodynamic equilibrium. A point describing state in wave on diagram p, V, moves along straight line

$$p = \varrho_0 D^2 (1 - \eta), \quad \eta = \frac{V}{V_0}, \tag{7.72}$$

where

$$p = A \varrho_0 \frac{T}{\eta} + \frac{4}{3} \frac{\sigma T^4}{c}. \tag{7.73}$$

Temperature and relative volume after the front of the wave T_1, η_1 are connected by equation of shock adiabat (in variables of temperature — volume), which during calculation of pressure and energy of radiation was in § 10, Chapter III (formula (3.76)). Let us copy it here in the form

$$\frac{A \varrho_0 T_1}{\eta_1} \left(\frac{\eta_1}{\eta_{10}} - 1 \right) = \frac{4 \sigma T_1^4}{3c} (1 - 7\eta_1), \tag{7.74}$$

where $\eta_{10} = (\gamma - 1)/(\gamma + 1)$ is final volume without taking into account density and radiation pressure. From this formula it is clear that at $p_{rad} \gg p_{gas}$ $\eta_1 = {}^1/_7$; at $p_{rad} \ll p_{gas}$ $\eta = \eta_{10}$.

Let us consider dependence of temperature on volume during compression of gas in the front of the wave, for which we will substitute expression (7.73) in equation of straight line (7.72):

$$A\varrho_0 \frac{T}{\eta} + \frac{4}{3}\frac{\sigma T^4}{c} = \varrho_0 D^2 (1-\eta).$$

This formula is more conveniently written otherwise, to replace in it $\rho_0 D^2$ through T_1 and η_1:

$$A\varrho_0 \frac{T}{\eta} + \frac{4}{3}\frac{\sigma T^4}{c} = \left(A\varrho_0 \frac{T_1}{\eta_1} + \frac{4}{3}\frac{\sigma T_1^4}{c}\right)\frac{1-\eta}{1-\eta_1}. \qquad (7.75)$$

Function $T(\eta)$ in interval $0 < \eta < 1$ has maximum (we will designate coordinates of maximum through T_{max}, T_{max}).

Radiation flux in wave S, as also in a case when density and radiation pressure are small, is directed always to one side, toward the flow of gas, and turns into zero only at $x = -\infty$ and $x = +\infty$, before and after front of wave. Therefore, temperature in the wave is obliged montonically to increase from initial $T = 0$ to final T_1, otherwise $S \sim - dT/dx$ would change sign inside wave.

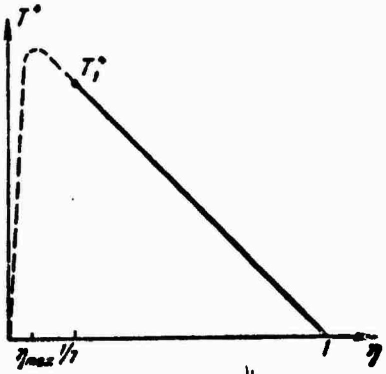

Fig. 7.29. T^4, η-diagram for shock wave with radiation in the absence of discontinuity.

If radiation pressure is small, $p_{rad} \ll p_{gas}$, then, as follows from formula (7.75), $\eta_{max} = 1/2 > \eta_1 \approx \eta_{10} = (\gamma - 1)/(\gamma + 1)$. Point on diagram T, η skips from one branch of curve $T(\eta)$ to another, passing maximum, and isothermal jump appears (see § 3, 17).

If however radiation pressure is great $p_{rad} \gg p_{gas}$, then point η_{max}, where function $T(\eta)$ passes through maximum, lies after interval of actually realized volumes $1/7 \approx \eta_1 < \eta < 1$: η_{max} is close to zero (this one may see from equation (7.75)). Thus, in this case density of gas in the wave changes continuously together with temperature, and discontinuity in the wave is lacking. This case is shown on diagram T^4, η (Fig. 7.29). Profiles of temperature, density of gas, and radiation flux in such a wave are depicted schematically in Fig. 7.30.

We will find amplitude of wave, at which discontinuity disappears. It, obviously, corresponds to such case, when point of maximum temperature T_{max}, η_{max} coincides with final point T, η_1 (exactly so as in § 3). Really, at $\eta_1 < \eta_{max}$ ("small" amplitudes) discontinuity exists; at $\eta_{max} < \eta_1$ ("large" amplitudes there is no discontinuity. Let us designate parameters of the front, corresponding to transition amplitude, differentiating regions of continuous solutions and isothermal jump through T,* η.*

Differentiating equation (7.75) for function T(η) and considering $dT/d\eta = 0$, $T = T$,* $\eta = \eta$,* and also considering in this equation and in equation of shock adiabat (7.74) $T_1 = T^*$ $\eta_1 = \eta$,* we will obtain a system of two equations for unknowns T,* η:*

$$\frac{AQ_0T^*}{\eta^{*2}} = \left(AQ_0\frac{T^*}{\eta^*} + \frac{4}{3}\frac{\sigma T^{*4}}{c}\right)\frac{1}{1-\eta^*},$$

$$\frac{AQ_0T^*}{\eta^*}\left(\frac{\eta^*}{\eta_{10}} - 1\right) = \frac{4\sigma T^{*4}}{3c}(1-7\eta^*).$$

Excluding from this system T,* we will obtain quadratic equation for η,* one of the roots of which, responding to real state is is equal to

$$\eta^* = \frac{1}{4+\sqrt{2+1/\eta_{10}}}. \qquad (7.76)$$

Thus, for instance, at $\gamma = 5/3$, $\eta_{10} = 1/4$, $\eta^* = 1/6.45$ (this value is somewhat larger than limiting volume during

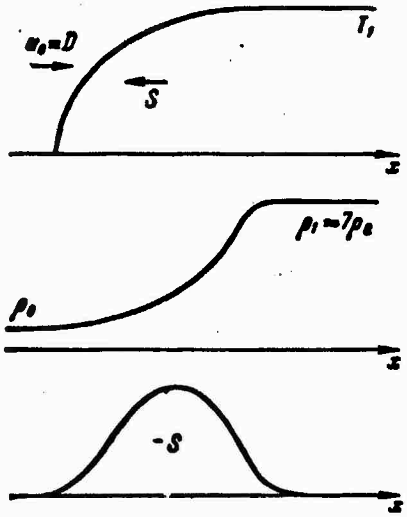

Fig. 7.30. Profiles of temperature, density of gas, and radiation flux in a shock wave, taking into account energy and radiation pressure in the case when jump is absent.

$p_{rad} \gg p_{gas}$, equal to 1/7). Transition amplitude, according to (7.74), corresponds to pressure ratio of radiation and the substance, in final state equal to $(p_{rad}/p_{gas})^* = \frac{4\sigma T^{*4}}{3c} \quad \frac{A\rho_0 T^*}{\eta^*} = 4.45$.

Let us note that with this amplitude speed of gas after the front, with respect to the front, is exactly equal to isothermal speed of sound in the final state (and during amplitudes larger than transition, when there is no discontinuity, speed of gas after the front is higher than isothermal speed of sound: the front moves with supersonic speed with respect to the gas after it).

The profile of temperature in a shock wave without discontinuity can be found, using, as usual, equations of hydrodynamics (7.40) and equation for flow of radiant thermal conduction $S = -\frac{cl}{3}\frac{d}{dx}\frac{4\sigma T^4}{c}$. We will not pause on this here.

In the work of V. S. Imshennik [51] is considered a shock wave in two-temperature plasma, taking into account radiation (temperatures of electrons and ions are not assumed identical).

Literature

1. L. D. Landau and Ye. M. Lifshits. Mechanics of solid matter, State Technical Press, 1954.

2. R. Becker. Z. f. Phys., 8, 321 (1922).

3. M. Morduchow and P. A. Libby. J. Aeron. Sci., 16, 674 (1949). Translation: Mechanics, No. 1 (1950).

4. L. Meyerhoff. J. Aeron. Sci., 17, 775 (1950). Translation: Mechanics, No. 6 (1951).

5. L. H. Thomas. J. Chem. Phys., 12, 449 (1944).

6. A. Herpin. Rev. Sci., 86, 35 (1948).

7. A. E. Puckett and H. J. Stewart. Quart. Appl. Mech., 7, 457 (1950).

8. R. Mises. J. Aeron. Sci., 17, 551 (1950). Translation: Mechanics, No. 3 (1951).

9. Lieber, Romano, and Lew. J. Aeron. Sci., 18, 55 (1951). Translation: Mechanics, No. 1 (1952).

10. P. Gilbarg and D. Paolucci. J. Rat. Mech. Annal., 2, 617 (1953).

11. J. Bernard. J. Aeron. Sci., 18, 210 (1951). Translation: Mechanics, No. 4 (1952).

12. M. Roy. C. R. Acad. Sci., 218, 813 (1944).

13. P. A. Libby. J. Aeron. Sci., 18, 187 (1951). Translation: Mechanics, No. 4 (1952).

14. K. Zoller. Z. f. Phys., 130, 1 (1951). Translation: Mechanics, No. 6 (1952).

15. G. R. Cowan and D. F. Hornig. J. Chem. Phys., 18, 1008 (1950); G. R. Cowan, E. F. Greene, and D. F. Hornig. J. Chem. Phys., 19, 427 (1951); E. F. Greene and D. F. Hornig. J. Chem. Phys., 21, 617 (1953).

16. H. M. Mott-Smith. Phys. Rev., 82, 885 (1951). Translation: Mechanics, No. 1 (1953).

17. A. Sakurai. J. Fluid Mech., 3, 3 (1957); Research, Rep. Tokyo Elect., Eng. College 5, 39 (1957); N 6, 49, 1958.

18. Rayleigh. Proc. Roy. Soc., 84, 247 (1910).

19. S. Chapman and T. Cowling. Mathematical theory of nonuniform gases, IL, 1960; D. A. Frank-Kamenetskiy. Diffusion and heat transfer in chemical kinetics, Publishing House of Academy of Sciences of USSR, 1947.

19a. V. Zhdanov, Yu. Kagan, and A. Sazykin. ZhETF 42, 857 (1962).

20. S. P. D'yakov. ZhETF, 27, 283 (1954).

21. F. S. Sherman. J. Fluid Mech., 8, 465 (1960).

22. T. G. Cowling. Phil. Mag., 33, 61 (1942).

23. Ya. B. Zel'dovich. ZhETF, 16, 365 (1946).

24. Ya. B. Zel'dovich. Theory of shock waves and an introduction to gas dynamics, Publishing House of Academy of Sciences of USSR, 1946.

25. W. Griffith, D. Brickl, and V. Blackman. Phys. Rev., 102, 1209 (1956).

26. V. H. Blackman. J. Fluid Mech., 1, 61 (1956).

27. O. Matthews. Phys. Fluids 2, 170 (1959). Translation: Problems of Rocket Technology, No. 11, 65 (1959).

28. S. A. Losev. DAN SSSR, 120, 1291 (1958).

29. N. A. Generalov and S. A. Losev. PMTF, No. 2, 64 (1960).

30. D. Britton, N. Davidson, W. Gehman, and G. Schott. J. Chem. Phys., 25, 804 810 (1956); H. B. Palmer and D. F. Hornig. J. Chem. Phys., 26, 98 (1957).

31. S. A. Losev and A. I. Osipov. UFN, 74, 393 (1960).

32. R. Duff and N. Davidson. J. Chem. Phys., 31, 1018 (1959). Translation: Problems of Rocket Technology, No. 5 (1960).

33. S. A. Losev and N. A. Generalov. DAN SSSR, 133, 872 (1960).

34. L. M. Biberman and B. A. Veklenko. ZhETF, 37, 164 (1959).

35. H. Petschek and S. Byron. Annals of Physics, 1, 270 (1957). Translation: Collection, Optical pyrometry of plasma, IL, 1960.

36. J. W. Bond. Phys. Rev., 105, 1683 (1957).

37. A. Rostagni. Nuovo Cimento, 13, 389 (1936).

38. Wayland. Phys. Rev., 52, 31 (1937).

39. H. D. Weymann. Phys. Fluids, 3, 545 (1960).

40. Y. Manheimer-Timnat and W. Low. J. Fluid Mech., 6, 449 (1959); B. Niblett and V. H. Blackman. J. Fluid Mech., 4, 191 (1958).

41. P. Hammerling, J. D. Teare, and B. Kivel. Phys. Fluids, 2, 422 (1959).

42. Ya. B. Zel'dovich. ZhETF, 32, 1126 (1957).

43. V. D. Shafranov. ZhETF, 32, 1453 (1957).

44. J. D. Jukes. J. Fluid Mech., 3, 275 (1957).

44a. D. A. Tidman. Phys. Rev. **111**, 1439 (1958).

45. O. W. Greenberg, H. K. Sen, and Y. M. Treve. Phys. Fluids, 3, 379 (1960).

46. M. Krook. Annals of Phys., 6, 188 (1959); J. W. Bond. Jet Propulsion 27, 228 (1958). Translation: Problems of Rocket Technology, No. 1 (1959).

47. Yu. P. Rayzer. ZhETF, 32, 1528 (1957).

48. Yu. P. Rayzer. ZhETF, 33, 101 (1957).

49. Ya. B. Zel'dovich and Yu. P. Rayzer. UFN, 63, 613 (1957).

50. V. A. Prokof'yev. Scientific notes of the Moscow State University, No. 172, Mechanics, p. 79 (1954).

50a. V. A. Belokon'. ZhETF, 36, 341 (1959).

51. V. S. Imshennik. ZhETF, 42, 236 (1962); Journal of Computational Mathematics and Mathematical Physics, 2, 206 (1962).

52. W. A. Gustafson. Phys. Fluids, 3, 732 (1960). Translation: Problem of Rocket Technology, No. 3, 31 (1961).

53. C. Muckenfuss. Phys. Fluids, 3, 320 (1960).

54. S. Ziering. Phys. Fluids, 4, 765 (1961).

55. P. Glansdorff. Phys. Fluids, 5, 371 (1962).

56. K. Hansen and D. F. Hornig. J. Chem. Phys., 33, 913 (1960).

57. P. A. Blythe. J. Fluid Mech., 10, 33, 1961, Collection of translations, Mechanics, No. 2, 69, 1962.

58. S. I. Anisimov. ZhETF, 31, 1491 (1961).

59. N. A. Generalov. Herald of Moscow State University, physical astronomy, No. 2, 51 (1962).

60. M. Camac. J. Chem. Phys., 34, 448 (1961).

61. W. Poth. J Chem. Phys., 34, 991 (1961).

62. D. L. Matthews. J. Chem. Phys., 34, 639 (1961).

63. N. H. Johannesen, H. K. Zienkiewicz, P. A. Blythe, and J. H. Gerrard. J. Fluid Mech., 13, 213 (1962).

64. L. R. Hurle and A. G. Gaydon. Nature, 4702, 184 (1959).

65. M. Camac. J. Chem. Phys., 34, 460 (1961).

66. J. P. Rink, H. T. Knight, and R. E. Duff. J. Chem. Phys., 34, 1942 (1961). Translation: Problems of Rocket Technology, No. 4, 58 (1962).

67. R. W. Patch. J. Chem. Phys., 36, 1919 (1962).

68. R. A. Allen, J. C. Keck, and J. C. Camm. Phys. Fluids, 5, 284 (1962).

69. K. Wray, J. D. Teare, P. Hammerling, and B. Kivel. 8th. Sympos. Internat. Combustion, Pasadena, 1960, 84.

70. Lin Shao-Chi. Rarefied Gas Dynamic, N. Y., London Acad. Press, 1961, 623.

71. Yu. S. Sayasov. PMTF, No. 1, 61, 1962; No. 6, 172 (1961).

72. N. M. Kuznetsov. Engineering-physics Journal, 3, 17 (1960); 5, No. 6, 97 (1962).

73. M. H. Bortner. Planet and Space Sci., 6, 74 (1961).

74. Yu. P. Lun'kin. ZhTF, 31, 1112 (1961).

75. W. Dorrance. J. Aero Space Sci., 28, 43, 1961. Translation: Problems of Rocket Technology, No. 9, 40 (1961).

76. L. Wetzel. Phys. Fluids 5, 824 (1962).

77. A. C. Pipkin. Phys. Fluids, 4, 1298 (1961).

78. M. H. Bortner. Planet and Space Sci., 3, 99 (1961).

79. V. H. Blackman and C. B. F. Niblett. Fundam. date obtained shock-tube exprim. Oxf. Lond, N. Y., Paris Pergamon Press, 221, 1961.

80. Lin Shao-Chi. Planet and Space Sci., 6, 94, 1961.

81. L. Lamb and Lin Shao-Chi. J. Appl. Phys., 28, 754 (1957). Translation: Problems of Rocket Technology, No. 3 (1958).

82. W. B. Sisco and J. M. Fiskin. Planet and Space Sci., 6, 47 (1961).

83. J. R . Viegas and T. C. Peng. ARS J. 31, 654 (1961).

84. A. Sherman. ARS J. 30, 559 (1960). Translation: Problems of Rocket Technology, No. 4, 21 (1961).

85. S. B. Pikel'ner. News of the Crimean Astrophysical Observatory, 12, 93, 1954; Fundamentals of space electrodynamics, Fizmatgiz, 1961.

86. S. C. Lin and J. D. Teare. Phys. Fluids, 6, 355 (1963).

87. S. C. Lin, R. A. Neal, and W. I. Fyfe. Phys. Fluids, 5, 1633 (1962).

CHAPTER VIII

PHYSICO-CHEMICAL KINETICS IN HYDRODYNAMIC PROCESSES

1. Dynamics of Nonequilibrium Gas

§ 1. Equations of Gas Dynamics in the Absence of Thermodynamic Equilibrium

In the preceding chapter, during the study of the structure of the front of a shock wave in gas with delayed excitation of certain degrees of freedom, we had the opportunity to meet one of the simplest problems of dynamics of nonequilibrium gas. Parameters after the front of a shock wave in a region where full thermodynamic equilibrium is established do not depend on the mechanism and speeds of nonequilibrium processes; however, the kinetics of these processes essentially affect the distribution of hydrodynamic magnitudes in a nonequilibrium region and its width. Distortions of gas-dynamic flows, introduced by nonequilibrium processes, are connected mainly with changes of heat capacity and effective adiabatic index of nonequilibrium gas, on which depends the course of the gas-dynamic process. It is possible to see the influence of the adiabatic index on gas-dynamic solutions in examples of those problems which were considered in Chapter I. Thus, during non-stationary expiration of gas from a pipe into a vacuum, exhaust velocity of earlier resting gas is equal to $u = \frac{2c_0}{\gamma - 1}$, where c_0 is speed of sound in initial state, $c_0 = (\gamma p_0/\rho_0)^{1/2}$. Let us assume that initially equilibrium diatomic gas, heated to such a temperature that in it vibrations are excited "classically," with the opening of a flap of a pipe is expanded so fast that vibrations remain frozen, and energy of vibrations during expansion cannot be turned into kinetic energy of expiration.*

This would signify that exhaust velocity corresponds not to equilibrium adiabatic index $\gamma = 9/7$ but to index $\gamma' = 7/5$, i.e., will be, roughly speaking, $7/5 = 1.4$ times less.

Already from this simplest reasoning one may see what considerable influence can be rendered by nonequilibrium of gas on dynamics of the process. The necessity of calculating the kinetics of the establishment of equilibrium appears whenever we have something to do with rapidly varying processes or with processes whose characteristic scales are comparable with "lengths" of relaxation.

One of the most important practical problems of such a type is the problem of flow, around a body, of strongly rarefied gas in which relaxation times are comparable with the time period for flowing around the body, i.e., "length" of relaxation is comparable with the characteristic dimensions of the body. During entrance into atmosphere of ballistic missiles with great supersonic speeds, before the body will be formed so-called forward shock, as is shown in Fig. 8.1. Distance of shock wave from front point of body is

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*During expansion, density of gas decreases, kinetic processes are delayed, and transition of vibrational energy into energy of translational thermal motion of molecules, which is necessary for subsequent transformation of the latter into energy of directed, hydrodynamic motion, is protected for a long time.

usually several or about ten times less than the radius of curvature of the front part of the body. If gas is so rarefied at that distance that it does not contain a very large number of gas kinetic mean free paths, then in the particles of gas after the front of the shock wave there cannot be excited slowly relaxing degrees of freedom, for instance, there cannot be established chemical equilibrium. Thanks to this the temperatures in the gas compressed by the shock wave turn out to be higher than during a condition of thermodynamic equilibrium, which changes conditions of heating of the body. Essentially, we deal here with a case when the character of gas-dynamic distributions is important in the nonequilibrium zone of the shock wave, appearing after the compression shock.

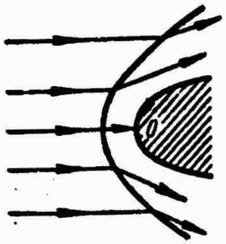

Fig. 8.1. Forward shock during supersonic flow around body.

In a number of problems an approximate description of the dynamics of nonequilibrium gas turns out to be possible by means of the use of a certain effective value of adiabatic index, corresponding to some degree of "freezing" of part of the heat capacity, for instance, when the change of energy in some degrees of freedom for characteristic hydrodynamic times in general can be disregarded.

In the general case it is necessary to consider the gas-dynamic process simultaneously with kinetics of nonequilibrium processes, which introduces a complication into the system of equations describing the phenomenon.

Dynamics of nonviscous and nonheat-conducting, thermodynamically equilibrium gas are described by equations of continuity, motion, and adiabatic nature:

$$\frac{d\varrho}{dt}+\varrho \operatorname{div}\bar{u}=0, \tag{8.1}$$

$$\varrho\frac{d\bar{u}}{dt}+\nabla p=0, \tag{8.2}$$

$$\frac{dS}{dt}=0, \tag{8.3}$$

to which is joined the thermodynamic connection of entropy with pressure and density: $S(p,\rho)$ (for instance, in gas with constant heat capacity $S = c_V \ln (p\rho^{-\gamma}) + \text{const}$).

We will be interested in the motion of gas whose state deviates from thermodynamic equilibrium. We will not, as before, consider viscosity and thermal conduction, considering that nonequilibrium is connected exclusively with delayed flow of internal processes, not going beyond the framework of a given particle of matter, let us say, delayed excitation of molecular vibrations.

In a nonequilibrium case, instead of the equation of adiabatic nature (8.3), which now is incorrect, one should use a more general equation expressing the law of conservation of energy; it is always accurate. Assuming that external sources of energy are absent,* we will record, instead of (8.3),

$$\frac{d\varepsilon}{dt}+p\frac{dV}{dt}=0. \tag{8.4}$$

In a state of thermodynamic equilibrium, equations (8.4) and (8.3) in virtue of thermodynamic identity

$$T\,dS=d\varepsilon+p\,dV \tag{8.5}$$

are equivalent. If in an equilibrium case internal energy ε is determined only by pressure and density, $\varepsilon = \varepsilon(p,\rho)$, then in the

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*Thermal effect of reversible chemical reaction is not external source of energy; it is considered by means of the introduction of a corresponding component in the expression for internal energy of gas.

absence of equilibrium it depends still on other parameters, characterizing the state of the system, which are not equilibrium (for instance, on degree of dissociation). Without specifying these parameters, we will call them λ.

In order to close the system of equations of gas dynamics, to equations (8.1), (8.2), and (8.4) one should join a relationship connecting internal energy with pressure, density, and parameters of state λ:

$$\varepsilon = \varepsilon(p, \rho, \lambda),$$

and also an equation of kinetics, which describes variations of parameters λ in a gas particle during time:

$$\frac{d\lambda}{dt} = f(\lambda, p, \rho).$$

Usually functions $\varepsilon(p, \rho, \lambda)$ and $f(\lambda, p, \rho)$ are expressed not directly through density and pressure, but with the help of temperature

$$\varepsilon = \varepsilon(\rho, T, \lambda), \quad \frac{d\lambda}{dt} = f(\lambda, \rho, T).$$

There is additionally introduced equation of state

$$p = p(T, \rho, \lambda).$$

Under temperature T, wherever this is not mentioned especially, is implied the temperature corresponding to translational degrees of freedom of molecules (atoms, ions), which usually are equilibrium even in the fastest gas-dynamic processes, since Maxwellian distribution of molecules in speeds is established extraordinarily fast.

Let us consider, as an example of a nonequilibrium system, diatomic gas without dissociation but with delayed excitation of molecular vibrations (we will not be interested in too high temperatures, at which degree of dissociation is still insignificantly small). Role of parameter λ is played by nonequilibrium energy of vibrations ε_{vib} (per 1 g of gas). The above-mentioned relationships, which one should add to system of equations (8.1), (8.2), (8.4), in this case it is possible to record in the form

$$\varepsilon = \varepsilon_1 + \varepsilon_{\text{к}} = \frac{5}{2} AT + \varepsilon_{\text{к}}, \tag{8.6}$$

$$p = A\rho T, \tag{8.7}$$

$$\frac{d\varepsilon_{\text{к}}}{dt} = \frac{\varepsilon_{\text{к}}(T) - \varepsilon_{\text{к}}}{\tau(T, \rho)}. \tag{8.8}$$

Here ε_1 is sum of energies of translational and rotational degrees of freedom of molecules (rotational energy is assumed to be equilibrium, i.e., corresponding to translational temperature T); $\varepsilon_{\text{vib}}(T)$ is energy of vibrations in thermodynamic equilibrium with translational degrees of freedom of molecules; $\tau(T, \rho)$ is relaxation time for establishment of vibrational equilibrium.

Analogous, but in form more complicated, it is possible to write equations for all other cases when there are nonequilibrium dissociations, chemical reactions, ionization or when translational temperatures of electron and atomic (ionic) gases differ. All these cases were examined in the preceding chapter when we examined the structure of the nonequilibrium layer in front of the shock wave.

§ 2. Growth of Entropy

A very important peculiarity of gas-dynamic processes in which gas is nonequilibrium is the growth of entropy of gas and dissipation of mechanical energy. As also with internal energy ε, the entropy of nonequilibrium gas is no longer determined by only two magnitudes: pressure and density or temperature and density, but depends on other parameters characterizing the nonequilibrium state: $S = S(p, \rho, \lambda)$ or $S(T, \rho, \lambda)$. Increase of entropy dS now is not equal to inflow of heat from external sources, divided by temperature, as in equilibrium case ($dS \neq dQ/T$). Entropy grows with time even in the absence of inflow of heat (when $dQ = 0$), only because of nonequilibrium internal processes.

et us explain this in the same example of nonequilibrium vibrations. Full specific entropy of gas S is composed of entropies corresponding to translational and rotational degrees of freedom, which in virtue of equilibrium it is possible to unite, and entropy of vibrations.* Let us designate these two parts of entropy through S_1 and S_{vib}:

$$S=S_1+S_{\text{к}}. \qquad (8.9)$$

For entropy of translational and rotational degrees of freedom it is possible to record thermodynamic identity:

$$T\,dS_1=d\varepsilon_1+p\,dV. \qquad (8.10)$$

Usually exchange of vibrational energy in molecules occurs much faster than exchange between vibrational and translational energies. Therefore, Boltzmann distribution with respect to vibrational excitations for molecules is established quite fast, and it is possible to ascribe to vibrations defined temperature T_{vib}. This temperature corresponds to actual reserve of vibrational energy of molecules $\varepsilon_{vib} = \varepsilon_{vib}(T_{vib})$; if one were to designate vibrational heat capacity c_{vib}, then $d\varepsilon_{vib} = c_{vib}dT_{vib}$. Of course, vibrational temperature T_{vib} can strongly differ from translational temperature of molecules T, which nonequilibrium of gas** consists of. If it is possible to ascribe to vibrations defined temperature T_{vib}, then for the vibrational part of entropy it is also possible to record

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*During nonequilibrium dissociations or ionizations one should record expression for entropy through numbers of particles of various sorts (molecules and atoms, for instance), which are not assumed to be equilibrium.

**We have already encountered a similar position in examining plasma. Maxwellian distributions and temperatures in electron and ionic gasses are established very fast. However, electron and ionic temperatures differ from each other due to deceleration of exchange of energy between electron and ionic gasses.

thermodynamic identity:

$$T_{\text{к}}\, dS_{\text{к}} = d\varepsilon_{\text{к}}. \qquad (8.11)$$

(energy and entropy of vibrations do not depend on volume of gas.)

It is easy to see that entropy of a nonequilibrium system only grows with time, independently of what kind of transformations the gas endures. Really, in virtue of equations (8.9), (8.10), (8.11), (8.4), (8.6) we have:

$$\frac{dS}{dt} = \frac{dS_1}{dt} + \frac{dS_{\text{к}}}{dt} = \frac{1}{T}\left(\frac{d\varepsilon_1}{dt} + p\frac{dV}{dt}\right) + \frac{1}{T_{\text{к}}}\frac{d\varepsilon_{\text{к}}}{dt} = \frac{d\varepsilon_{\text{к}}}{dt}\left(\frac{1}{T_{\text{к}}} - \frac{1}{T}\right). \qquad (8.12)$$

Taking into account equation of kinetics (8.8), in which

$$\varepsilon_{\text{к}} = \int_0^{T_{\text{к}}} c_{\text{к}}(T')\, dT', \text{ and } \varepsilon_{\text{к}}(T) = \int_0^{T} c_{\text{к}}(T')\, dT',$$

we see that at $T_{vib} < T$ vibrations remove energy from translational and rotational degrees of freedom, $\frac{d\varepsilon_{vib}}{dt} > 0$ and $\frac{dS}{dt} > 0$. At $T_{vib} > T$ oscillations return their energy $\frac{d\varepsilon_{vib}}{dt} < 0$, but, as before, $\frac{dS}{dt} > 0$. The considered example illustrates the second law of thermodynamics, according to which without participation of external influences heat is always transmitted from a more heated object to a less heated one, as a result of which entropy of all the system is increased. In this case the "objects" are not touching bodies, but different degrees of freedom of one and the same body.

If at some moment the gas was in thermodynamic equilibrium, then participated in a fast-flowing process during which equilibrium in it was disturbed, and then entered into a region of slow changes of state, in order to again come into equilibrium, entropy is increased in the gas.

Increase in entropy of gas is accompanied by dissipation of mechanical energy, irreversible transformation of it into heat.

If the process takes place without participation of external sources of energy, conforming to equation of energy (8.4), then dissipated energy cannot again be turned into mechanical energy ever under any kind of conditions.

The phenomenon of dissipation we will meet more specifically in the following paragraph when examining sound absorption in a relaxing medium. Absorption of sound waves constitutes a characteristic example of the dissipation of mechanical energy. An example of incomplete use of energy due to "irreversibility" can be the above-considered idealized case of expiration of gas into a vacuum with completely frozen vibrations. Into kinetic energy of momentum goes only the "reversible" part of internal energy: the energy of translational and rotational degrees of freedom, but the energy of vibrations thus will remain in molecules, thanks to which the exhaust velocity turns out to be smaller. Similar effects of irreversibility in the presence of nonequilibrium processes can lead to additional losses in high-speed turbines at high temperatures, in nozzles of rocket engines, etc. On the use of the effect of increase of entropy with time is based the independent method of measuring time of vibrational relaxation τ applied by Kantrowitz [1] for investigation of relaxation in CO_2.

To gas-dynamic calculations, taking into account nonequilibrium processes pertaining mainly to the problem of flowing around and aerodynamic heating of bodies entering the atmosphere (satellites, ballistic missiles), is dedicated extensive literature (see, for instance [2, 2a]; in the same place are reference to many other works). We will not remain here on questions of the reverse influence of physical chemical kinetics on gas dynamics of processes.

We will interest ourselves in this chapter with other question: the kinetics of nonequilibrium processes not from the point of view of its influence on the motion of gas, but from the point of view of determining concentrations of different components under conditions of an essentially nonequilibrium course of chemical reactions, ionization, condensation of vapors in different hydrodynamic phenomena. Hydrodynamics, as a rule, will be considered in approximate form by means of the use of certain effective values of adiabatic index, and to an already known hydrodynamic solution will be "added" kinetics of interesting processes.

The only exception will be the following two paragraphs, in which there will be considered the phenomena of absorption and dispersion of sound in a relaxing medium (i.e., there will be studied the influence of nonequilibrium processes on the gas-dynamic process — the propagation of sound waves).

§ 3. Anomalous Dispersion and Absorption of Ultrasonics

Usually noticeable, dispersion and sound absorption in gases, connected with viscosity and thermal conduction, appear only during very small lengths of sound waves, comparable with the mean free path of particles in gas, and frequencies comparable with the frequency of gas kinetic collisions (see § 22 Ch. I).

However, during propagation of ultrasonic waves in molecular gases, sometimes are observed anomalous high dispersion and absorption in a region of much larger wave lengths and smaller frequencies. These phenomena are connected with relaxation processes of establishment of equilibrium in slowly excited degrees of freedom of gas. In limiting case of low frequencies, relaxation times for establishment of equilibrium in those degrees of freedom which give a noticeable contribution to heat capacity are small as compared to period of sound vibrations. In these conditions the state of a particle of gas at each moment is a state of thermodynamic equilibrium and "follows" changes of pressure and density in sound wave.

Speed of sound, equal to the square root of adiabatic derivative from pressure with respect to density, corresponds to its own thermodynamically equilibrium value:

$$a^2 = \left(\frac{\partial p}{\partial \varrho}\right)_S = \gamma \frac{p_0}{\varrho_0}, \quad \gamma = \frac{c_p}{c_V} = 1 + \frac{A}{c_V}{}^{*}. \tag{8.13}$$

Conversely, in a limiting case of very high frequencies, slowly relaxing degrees of freedom cannot be excited in a sound wave; their energy simply corresponds to temperature of undisturbed state T_0. These degrees of freedom do not participate in periodic change of the state of the gas; they are "frozen" and do not affect adiabatic connection of changes of pressure and density. The active part of heat capacity now is less than equilibrium; the adiabatic index and speed of sound is larger than at low frequencies.

In the intermediate region of frequencies there occurs gradual change of speed of sound from equilibrium value a_0 to value a_∞, corresponding to the "frozen" part of heat capacity, i.e., dispersion appears. Thus, for instance, measurement of Kneser [3, 4] showed that speed of sound in carbon dioxide at room temperature changes from $a_0 = 260$ m/sec at frequency ν of the order of 10^4 sec^{-1} (10 kilocycles) to $a_\infty = 270$ m/sec at $\nu \sim 10^6$ sec^{-1} (1 Mc.). The low speed of sound corresponds to equilibrium value of heat capacity:

$$c_V = c_{\text{пост}} + c_{\text{вращ}} + c_{\text{кол}} = \frac{3}{2}A + A + 0,8A = 3,3A$$

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*We use always specific heat capacities; A is gas constant, calculated per 1 g. In avoiding confusion, speed of sound here we will designate by letter a instead of c.

(a CO_2 molecule is linear, so that $c_{rot} = A$; at room temperature are excited only low-frequency vibrations of a molecule with $c\ h\nu/k = 954^{0}K$, where vibrational heat capacity is still less than its classical value A). High speed of sound corresponds to frozen vibrations, i.e., heat capacity $c_V = c_{trans} + c_{rot} = 2.5$ A. From these measurements it follows that relaxation time for excitation of vibrations in a CO_2 molecule (during atmospheric pressure) corresponds to a certain intermediate frequency of sound, and namely $\tau_{vib} \sim 1/\nu \sim 10^{-5}$ sec. Rotations in molecules at room temperature are excited very fast and dispersion, connected with delayed excitation of rotations, could be observed at atmospheric pressure only at extraordinarily large frequencies $\nu \sim \frac{1}{\tau_{rot}} \sim 10^9 - 10^{10}$ sec^{-1} (only exception is hydrogen; see § 2 Ch. VI).

Dispersion of sound is observed even in gases in which occur slow chemical transformations during changes of temperature (and density) in sound wave. An example can be the reaction of polymerization of nitrogen peroxide $2NO_2 \leftrightarrows N_2O_4$, which occurs lightly at room temperature, since heat of its activation in both directions is small. It was in reference to just such systems that the theory of dispersion of sound was for the first time developed by A. Einstein in 1920 [5]. Apparently, analogous phenomena occur also during propagation of untrasonics in certain liquids.

Measurement of dispersion and absorption of ultrasonics is one of the most important methods of studying relaxation processes and experimental determination of relaxation times. To this question is dedicated much literature,* and we will not here discuss it. In detail, let us pause only on basic physical peculiarities and regularities of the phenomenon.

Dispersion of sound in a relaxing substance is always accompanied by raised absorption, which considerably exceeds "natural" absorption because of usual viscosity and thermal conduction. In a sound wave a particle of matter accomplishes consecutive cyclical transformations, returning, upon completion of each cycle, to initial state. If in the particle there occur internal nonequilibrium processes, then they inevitably lead to increase of entropy, dissipation of mechanical energy, i.e., to sound absorption. It is necessary to emphasize that in the presence of dissipation the state of the particle, upon completion of the cycle, somewhat differs from the initial state (since entropy of it is increased).

However, this distinction, let us say, increase of temperature proportional to increase of entropy, is a magnitude of the second order of smallness with respect to the low amplitude of sound wave Δp or ΔT, inasmuch as increase of entropy ΔS is proportional to sound energy, which in turn is proportional to $(\Delta p)^2$ (see § 3, Ch. I). Therefore, in the first approximation motion in a sound wave, even in the presence of absorption, is adiabatic and it is possible to consider the cycles as closed.

The process of dissipation of mechanical energy and sound absorption is easy to comprehend, considering a cycle in gas on diagram p, V. In Fig. 8.2 is conducted two families of adiabats, one

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*Survey of it and references can be found, for instance, in [6].

of which (I) corresponds to equilibrium changes of state, and the other (II) to the frozen part of heat capacity. Adiabats are conducted near an undisturbed state of gas, designated by point 0. During very slow sound vibrations, a point describing state of gas p, V, oscillates near the center 0 along one (equilibrium) adiabat, designated in Fig. 8.2 as I'. In a limiting case of very high frequency the point oscillates near the center along one "frozen" adiabat, designated by II'. And in either case nonequilibrium processes do not occur; entropy of gas does not change and sound absorption is lacking. Work accomplished upon the gas for the cycle, numerically equal to the area of a figure described by the point on the diagram p, V, is equal to zero, as to which the absence of absorption attests. The fact that in the second case entropy of gas, in thermodynamic equilibrium as in the first case, does not change, is easy to see in the example of vibrational relaxation. As can be seen from formula (8.12), speed of change of entropy in nonequilibrium process is proportional to speed of change of vibrational energy. But during strictly frozen vibrations their energy in general, does not change, ε_{vib} = const and $dS/dt = 0$.

We will consider now sound waves of intermediate frequencies, with which the course of relaxation processes is essential (For definitiveness again we consider vibrational relaxation). For simplicity we will present that a sound wave has the unique, step profile of density, depicted

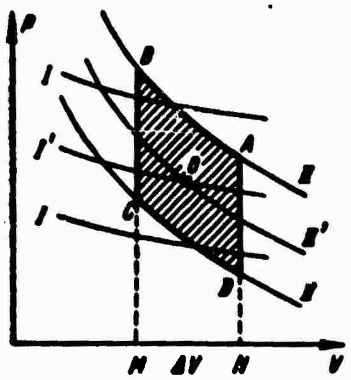

Fig. 8.2. p, V-diagram for a cycle in a sound wave with rectangular profile.

in Fig. 8.3a.*

In this graph it is possible to consider as distribution of density with respect to a coordinate at a given moment of time or as the law of density change in a given particle of gas in time. The same pertains also to Fig. 8.3b, on which is shown a corresponding profile of temperature (or pressure; profiles of temperature and pressure in this case are similar to each other).

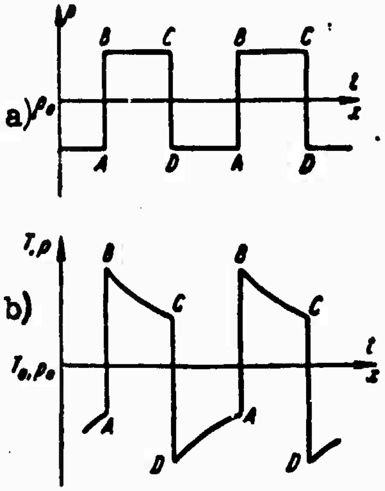

Fig. 8.3. Acoustic wave in a relaxing gas with step profile of density. a) profile of density; b) profile of temperature.

We will trace the change of state of a particle in a wave both on diagram p, V, Fig. 8.2, and in Fig. 8.3a and b. During very fast compression of gas from point A to point B, its state changes along "frozen" adiabat II. Entropy does not change, on the gas is accomplished positive work, numerically equal to area NABM. Temperature and pressure of gas sharply increase, and vibrational energy remains constant, corresponding to old, low temperature. Then during a certain time density of gas remains constant (transition B → C). There occurs excitation of vibrations; part of the energy is taken away from translational and rotational degrees of freedom; temperature and pressure drop, entropy increases (see formula (8.12): $T_{vib} < T$, $d\varepsilon_{vib}/dt > 0$, $dS/dt > 0$).

Inasmuch as volume of gas does not change, work in the period of transition B → C is not accomplished.

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*This example, possessing great clarity, was considered earlier, for instance, in the book of G. S. Gorelik [7].

Further, gas is very fast expanded (transition C → D) along "frozen" adiabat II. Temperature and pressure drop; entropy does not change; vibrational energy also does not change, preserving its own value obtained by moment C. Gas accomplishes work numerically equal to area MCDN (above gas is accomplished negative work). And, finally, during slow transition D → A at constant volume, vibrations are partially deactivated since their energy exceeds value corresponding to falling temperature; vibrational energy partially passes into translational and rotational energy; temperature and pressure increase; entropy also increases ($T_{vib} > T$, $d\varepsilon_{vib}/dt < 0$, $dS/dt > 0$). Work, with this, is not accomplished.

Thus, in stage of expansion C → D a gas particle performs over the surrounding gas less work than would be accomplished by the surrounding gas above it in stage of compression A → B; particle "returns back" to work not completely. Part of the energy expended in the period of compression "forever" remains in it.

This energy, numerically equal to the difference of works, i.e., area of figure ABCD, constitutes mechanical energy irreversibly passing over into heat. In accordance with dissipation of mechanical energy sound wave is weakened (is absorbed), where absorption of energy of sound for the period (or on the wave length) is exactly equal to area ABCD.

On the other hand, irreversible liberation of heat is connected with increase of entropy after the cycle: it is equal to $T_0\Delta S$. This magnitude, as can be seen from Fig. 8.2, is proportional to $\Delta V \cdot \Delta p \sim (\Delta p)^2$. It follows from this that displacement of point of final state A' with respect to point of initial state A $\delta p = (\partial p/\partial S)_V \cdot \Delta S \sim (\Delta p)^2$ is a magnitude of the second order of smallness with respect to amplitude Δp. Inasmuch as $(\partial p/\partial S)_V > 0$, $\delta p > 0$, i.e., pressure after termination of cycle is slightly higher than initial. Exactly so is temperature slightly higher: $\delta T = \left(\frac{\partial T}{\partial S}\right)_V \Delta S = \frac{T\Delta S}{c_V} \approx \frac{T_0\Delta S}{c_V}$. Increase of temperature is equal to energy which is dissipated after cycle, divided by heat capacity at constant volume.

In a sinusoidal (harmonic) sound wave, point on diagram p, V describes a curve. All parameters of state — density, pressure, and temperature — change with the course of time by harmonic law. However, due to delayed excitation and deactivation of vibrations in molecules, changes of temperature of pressure do not manage to follow changes of density, and sinusoid of pressure is shifted in phase with respect to sinusoid of density (volume). It is possible to show that the point on diagram p, V describes an elliptic trajectory, where the axes of ellipse are inclined with respect to axes of coordinates p, V.

At small frequencies ν (or "circular" frequencies $\omega = 2\pi\nu$) the ellipse will stretch along equilibrium adiabat (see Figure 1 in Fig. 8.4). The thickness of it in the limit of small frequencies is proportional to frequency (to first member of expansion with respect to small magnitude ω). Energy of sound, absorbed for the period, is proportional to ω, and for unit of time is proportional to number of cycles i.e., to ω^2. At large frequencies, the ellipse will stretch about the "frozen" adiabat (Figure 2). Its thickness also, because of expansion is proportional to $1/\omega$, and absorption in a unit of time is proportional to $\omega \cdot 1/\omega$, i.e., does not depend on frequency. The biggest absorption for the period occurs in an intermediate case, when frequency is of an order reverse to time of relaxation. The ellipse, with this, has the biggest thickness (Figure 3); this thickness is of the order of vertical distance between equilibrium and "frozen" adiabats during maximum change of pressure, equal to amplitude of wave (distance between points Q and Q' in Fig. 8.4). If the relative difference of equilibrium and "frozen" indices of adiabat is great (namely it is characterized by angle between adiabats I and II, i.e., distance QQ'), then thickness of the ellipse can even become of the order of its length. This corresponds to a large shift in phase between pressure and density of the order of $\pi/2$ (if ellipse were turned into a circle, shift in phase would become exactly equal to $\pi/2$).

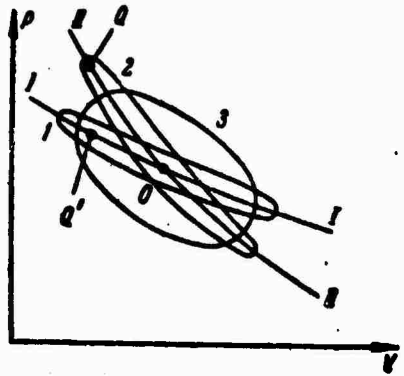

Fig. 8.4. p, V-diagram for cycles in harmonic sound waves of different frequency.

§ 4. Law of Dispersion and Coefficient of Absorption of Ultrasonics

Presented in the preceding paragraph, qualitative considerations with respect to dispersion and sound absorption in the presence of relaxation processes in a substance are covered in elegant mathematical form. In the common form, this was done by L. I. Mandel'shtam and M. A. Leontovich [8]*; formulas for dispersion and absorptions, including relaxation time τ, serve usually for experimental determination of this time on curves of dispersion or absorption, measured by experiment depending upon ultrasonic frequency.

We will show how it is possible to conclude the law of dispersion and the coefficient of sound absorption in a relaxing medium. For simplicity and clarity all calculations will be made on a concrete example of gas with nonequilibrium vibrations, for which in § 1 was formulated a full system of equations of gas dynamics (8.1), (8.2), (8.4), (8.6), (8.7), (8.8). Let us record all variables in a sound wave — pressure, density, etc. — in the form $f = f_0 + f'$, where f_0 is mean value corresponding to undisturbed gas, and f' is variable part which we will consider a small magnitude (speed $u = u_0 + u' = u'$; since undisturbed gas is at rest: $u_0 = 0$). Actual energy of vibrations it is also possible to present in the form $\varepsilon_{vib} = \varepsilon_{vib\,0} + \varepsilon'_{vib}$, where ε_{vib0} is vibrational energy in undisturbed gas, which, naturally, is in equilibrium. Variable part of equilibrium vibrational energy we will record in the form $\varepsilon'_{vib}(T) = c_{vib}T'$, where c_{vib} is vibrational heat capacity, corresponding to average temperature T_0 (if at temperature T_0 vibrations are classical, $c_{vib} = A$; otherwise c_{vib} is expressed by quantum formula (see § 2

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Ch. III)).

Let us place in the equations all magnitudes in the shown form, and we will disregard members of the second order of smallness, i.e., we will linearize the equation, as is done in acoustics (see § 3 Ch. I). Let us obtain, in a one-dimensional flat case, a system of equations for variables of parts of the magnitudes:

$$\left.\begin{array}{ll} \dfrac{\partial \rho'}{\partial t} + \rho_0 \dfrac{\partial u'}{\partial x} = 0, & \varepsilon' = \dfrac{5}{2} AT' + \varepsilon'_{\text{K}}, \\ \dfrac{\partial u'}{\partial t} + \dfrac{1}{\rho_0} \dfrac{\partial p'}{\partial x} = 0, & \dfrac{p'}{p_0} = \dfrac{T'}{T_0} + \dfrac{\rho'}{\rho_0}, \\ \dfrac{\partial \varepsilon'}{\partial t} - \dfrac{p_0}{\rho_0^2} \dfrac{\partial \rho'}{\partial t} = 0, & \dfrac{\partial \varepsilon'_{\text{K}}}{\partial t} = \dfrac{c_{\text{K}} T' - \varepsilon'_{\text{K}}}{\tau}. \end{array}\right\} \quad (8.14)$$

Here, in equation of energy (8.4), instead of specific volume density is introduced, but both parts of the equation of state are divided by $p_0 = A\rho_0 T_0$. Relaxation time τ is considered constant and equal to $\tau = \tau(T_0, \rho_0)$.

We will look for solution of system (8.14) in the form of a harmonic plane wave, recording all magnitudes in the form

$$f' = f'^{*} e^{-i(\omega t - kx)}. \quad (8.15)$$

Wave number k in general is complex: $k = k_1 + ik_2$. Real part k_1 constitutes reciprocal length of wave $k_1 = 1/\lambda$ and determines actual speed of sound — phase speed of propagation of wave $a_1 = \omega/k_1$; imaginary part k_2 gives coefficient of sound absorption:

$$f' = f'^{*} e^{-i\omega\left(t - \frac{x}{a_1}\right)} e^{-k_2 x}. \quad (8.16)$$

Magnitude $a = \omega/k$ it is possible to call complex speed of sound.

Amplitudes f'^{*} in general also are complex: $f'^{*} = |f'^{*}| e^{i\varphi}$. The complex character of amplitudes testifies to a shift in phase of some magnitudes relative to others (by difference of angles φ).

Putting in equations (8.14) all magnitudes in the form (8.15) and noticing that $\frac{\partial f'}{\partial t} = -i\omega f'$, $\frac{\partial f'}{\partial x} = ikf'$, we will obtain a system of algebraic equations for shaded magnitudes (or amplitudes, if one were to reduce by exponential factor):

$$\left.\begin{aligned} -i\omega\rho' + \rho_0 iku' &= 0, & \varepsilon' &= \frac{5}{2}AT' + \varepsilon'_{к}, \\ -i\omega u' + \frac{1}{\rho_0} ikp' &= 0, & \frac{p'}{p_0} &= \frac{T'}{T_0} + \frac{\rho'}{\rho_0}, \\ -i\omega\varepsilon' + \frac{p_0}{\rho_0^2} i\omega\rho' &= 0, & -i\omega\varepsilon'_{к} &= \frac{c_{к}T' - \varepsilon'_{к}}{\tau}. \end{aligned}\right\} \tag{8.17}$$

The last equation, being solved relative to ε'_{vib}, gives

$$\varepsilon'_{к} = \frac{c_{к}T'}{1 - i\omega\tau}. \tag{8.18}$$

Namely thanks to this complex connection of variables of parts of actual vibrational energy and temperature there appear dispersion and absorption. Already from this it is clear that in limiting cases $\omega\tau \to 0$, and $\omega\tau \to \infty$, when $\varepsilon'_{vib} = c_{vib}T'$ and $\varepsilon'_{vib} = 0$, imaginary unit completely falls from system of equations (8.17); all magnitudes are real (if under p', ρ' etc., we understand amplitudes p'^*, ρ'^* etc.). There are no absorptions and shifts in phase with this.

The first two equations of system (8.17), which were obtained from equations of continuity and motion after excluding speed, give the usual connection:

$$p' = \frac{\omega^2}{k^2}\rho' = a^2\rho', \tag{8.19}$$

where a is complex speed of sound. Excluding from the remaining four equations ε', ε'_{vib}, and T', we will find one more connection of p' and ρ':

$$p' = \gamma\frac{p_0}{\rho_0}\rho', \quad \gamma = \frac{\frac{7}{2}A + \frac{c_{к}}{1 - i\omega\tau}}{\frac{5}{2}A + \frac{c_{к}}{1 - i\omega\tau}}. \tag{8.20}$$

Magnitude γ it is possible to call a complex adiabatic index. Let us introduce designations: $c_{V0} = \frac{5}{2}A + c_{vib}$, $c_{p0} = \frac{7}{2}A + c_{vib}$ are equilibrium heat capacities during constant volume and pressure and $c_{V\infty} = \frac{5}{2}A$, $c_{p\infty} = \frac{7}{2}A$ are heat capacities during completely frozen vibrations. We will record complex adiabatic index and expression for complex speed of sound, which follows from equations (8.19), (8.20), in the form

$$a^2 = \gamma \frac{p_0}{\rho_0}, \quad \gamma = \frac{c_{p_0} - i\omega\tau c_{p_\infty}}{c_{V_0} - i\omega\tau c_{V_\infty}} \text{*)}. \qquad (8.21)$$

In limiting case of small frequencies $\omega\tau \ll 1$, $\gamma = \frac{c_{p0}}{c_{V0}} = \gamma_0$, $a^2 = \gamma_0 \frac{p_0}{\rho_0} = a_0^2$, we obtain equilibrium adiabatic index and speed of sound.

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*In the book L. D. Landau and Ye. M. Lifshits [9] there is derived an excellent formula (Ch. VIII, § 78, formula (78.3)), which gives

$$\gamma = \frac{1}{1 - i\omega\tau}\left[\frac{c_{p_0}}{c_{V_0}} - i\omega\tau \frac{c_{p_\infty}}{c_{V_\infty}}\right].$$

This divergence is connected with the difference in determinations of relaxation time τ, which appears in the equation of kinetics. Magnitude $\varepsilon_{vib}(T)$ in our equation (8.8) constitutes equilibrium energy of vibrations, which corresponds to translational temperature T. Let us note relaxation time in our equation of kinetics by index "T." If volume of gas is constant and translational temperature also is maintained constant: T = const, then equation (8.8) gives exponential law of approximation to equilibrium with characteristic time τ_T:

$$\varepsilon_K = \varepsilon_K(T) + [(\varepsilon_K)_{t=0} - \varepsilon_K(T)] \exp\left(-\frac{t}{\tau_T}\right).$$

Energy of gas $\varepsilon = c_{V_\infty} T + \varepsilon_{vib}$ with this, is not constant.

If, however, we consider energy ε constant (and, of course, volume) and use equation (8.8), then we will obtain, instead of simple exponential law, a more complicated law of approximation to equilibrium.

In book [9] the equation of kinetics of type (8.8) is recorded in such a way that under equilibrium one should understand energy of vibrations, which corresponds to equilibrium temperature T_p, common for translational and vibrational degree of freedom and responding to given volume V and energy ε of gas.

Let us designate relaxation time, which appears in equation of kinetics (according to [9]), by τ_S. An equation gives exponential law of approximation to equilibrium:

$$\varepsilon_K = \varepsilon_K(T_p) + [(\varepsilon_K)_{t=0} - \varepsilon_K(T_p)] \exp\left(-\frac{t}{\tau_S}\right),$$

if volume, energy of gas, i.e., equilibrium temperature T_p, and time τ_S are constant (actually τ_S depends on translational temperature, but it is assumed that deflection from equilibrium is small, so that at T_p = const translational temperature T changes little. During small deflection from equilibrium condition V = const, ε = const it is possible to consider as condition of approximate constance of entropy S ≈ const).

Footnote continued on following page

Experiments, in which there is obtained a gas cloud scattering into a vacuum, were set up during rocket investigations of the upper layers of the atmosphere, when into space were released vapors of sodium and nitric oxide. The same phenomenon took place also during creation of artificial comet during flight to Moon of Soviet space rocket.

Dynamics of the scattering of a gas cloud into a vacuum is rather simple; an idealized problem about adiabatic scattering into vacuum of a gas sphere, when gas possesses constant heat capacity, was considered in §§ 28 and 29, Ch. I. Here we are interested in more delicate questions of the state of gas in a stage of large expansion, so to say, during scattering into infinity, which it is possible to consider on the basis of the most simple diagram of scattering. In this diagram is taken into account the behavior of only average in mass parameters of gas. It is clear that parameters of any specific particle of gas change in time exactly as average magnitudes, and differ from mean values only by numerical factors of the order of unity, which for us are immaterial.

Let us consider a gas sphere of mass M, possessing energy E.* In the stage of strong expansion almost all initial energy has already been turned into kinetic energy of scattering, and

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*We, for convenience, will remember here certain conclusions in § 28, Ch. I.

Coefficient of absorption $k_2 \sim \omega^2$; absorption at a distance equal to wave length, $k_2\lambda \sim \omega$.

In the limit of large frequencies $\omega\tau \gg 1$ we have

$$k = k_1 + ik_2 = \frac{\omega}{a_\infty} + i\frac{1}{2a_\infty\tau}\frac{c_{p0}}{c_{p\infty}}\left(\frac{\gamma_\infty}{\gamma_0} - 1\right). \tag{8.23}$$

Coefficient of absorption $k_2 \approx$ const does not depend on frequency; absorption on wave length $k_2\lambda \sim 1/\omega$.

Curve of dispersion $a_1(\omega)$ and frequency dependence of absorption on wave length $k_2\lambda = k_2a_1/\omega = k_2/k_1$ are schematically depicted in Fig. 8.5. It is simple to show that magnitude k_2/k_1 has maximum at $\omega\tau = \sqrt{c_{V_0}c_{p_0}/c_{V\infty}c_{p\infty}} \sim 1$. During a close but different value of $\omega\tau$ the curve of dispersion has a bend.

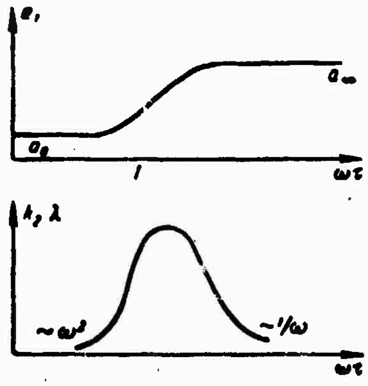

Fig. 8.5. Dependences of speed of propagation a_1 and coefficient of absorption on wave length $k_2\lambda$ of ultrasonics in the region of relaxation.

From formula (8.19) it follows that pressure in the sound wave is shifted in phase with respect to density. Really, if the speed of sound is a complex value, then $p' = a^2\rho' = |a^2|e^{i\varphi}\rho'$. In limiting cases $\omega\tau \ll 1$ and $\omega\tau \gg 1$, when the imaginary part of the speed of sound aspires to zero, shift in phase φ disappears. At $\omega\tau \sim 1$, when the real and imaginary parts are comparable, shift in phase φ is considerable.

If in the substance there occurs several nonequilibrium processes with strongly differing times of relaxation, strong absorption and dispersion appear every time when $\omega\tau \sim 1$, and these frequency ranges clearly are divided. In the case of close relaxation times regions merge and are experimentally divided, i.e., to extract relaxation times from experimental data is very difficult.

Dispersion and absorption of sound, connected with nonequilibrium processes, are determined by vibrations of density of substance, i.e., in virtue of equation of continuity $d\rho/dt + \rho \mathrm{div}\, u = 0$ are connected with divergence of speed. Formally, it is possible to describe them by a coefficient of second viscosity ζ, which characterizes the dissipative member in the equation of motion, proportional to the divergence of speed (see § 20 and 21, Ch. I). The coefficient of second viscosity it is possible formally to connect with magnitude $\omega\tau$ and with limiting velocities of sound a_0 and a_∞ (see, for instance, [9]).

However, it is possible to describe anomalous absorption by means of the introduction of a coefficient of second viscosity only at not too large frequencies. Coefficient of absorption, because of viscosity, grows proportionally to $k_2 \sim \omega^2$ (see § 22, Ch. I). Therefore, during $\omega \to \infty$ absorption, connected with viscosity, increases without limit, then, as in reality, coefficient of anomalous absorption during $\omega \to \infty$ aspires to constant: $k_2 = \mathrm{const}$ (see formula (8.23)).

Certain experimental data on relaxation times for excitation of vibrations and rotations in molecules, obtained by studying dispersion and absorption of ultrasonics, already were presented by us in §§ 2 and 4, Ch. VI.

2. Chemical Reactions

§ 5. Oxidation of Nitrogen During a Strong Explosion in Air

Atmospheric air consists of molecules of nitrogen and oxygen; chemically it is in equilibrium and very stable. For dissociation of molecules into atoms or partial transformation of them into molecules of nitric oxide NO it is necessary to heat air to several thousand degrees. Reaction of the oxidation of nitrogen requires great activation energy. Somewhat less, but also great, is the activation energy necessary for disintegration of molecules of oxide into oxygen and nitrogen. Therefore, independent of the energy advantage of the transformation of nitric oxide into oxygen and nitrogen at low temperatures, molecules of oxide NO are extraordinarily stable with respect to disintegration.

In § 8 Ch. VI it was shown that if at a temperature of 4000° K time of establishment of equilibrium concentration of nitric oxide in air of normal density is $\sim 10^{-6}$ sec., then at 2000° K it is equal to approximately 1 sec. and at 1000° K has a colossal magnitude of the order of 10^{12} sec., i.e., approximately 30 thousand years! Once formed and cooled to normal temperature, nitric oxide remains in the air an indefinitely long time. In reality, oxidized nitrogen continues its prolonged existence in the form of dioxide NO_2 (or even groups of N_2O_4, in which molecules of NO_2 prefer to be united), since nitric oxide reacts very fast with atmospheric oxygen and is oxidized to dioxide. This exothermic reaction requires very small activation energy and occurs easily even at room temperature (see § 9 Ch. VI).

Thus, the chemical process in heated, and then cooled, air leads to essentially nonequilibrium states, found in sharp contradiction with the laws of chemical equilibrium, according to which nitric oxides at low temperatures must be completely turned into nitrogen and oxygen. This effect, well-known from laboratory practice, carries the name of the "hardening" effect of oxides of nitrogen.

Large quantity of nitric oxides will be formed during a strong explosion in air. Atmospheric nitrogen is oxidized in that stage of the process when air in the blast wave is heated to a temperature of several thousand degrees, where several percents of nitrogen is oxidized. During propagation of the blast wave, air originally heated in the front of the shock wave is rapidly cooled. Nitric oxide formed in it does not succeed in disintegrating during cooling and remains in the air "forever." During an explosion with energy of 10^{21} erg, equivalent to approximately 20,000 tons of trotyl, in the air will be formed nearly 100 tons of nitric oxides. Several tens of seconds or a minute after termination of explosion all oxide is turned into dioxide.

In the usual state nitrogen peroxide constitutes of a sharply colored gas of a reddish-brown color which is connected with the predominant absorption by NO_2 molecules of green and blue rays. It gives a red shade to the cloud which rises upward after termination of explosion,* as was noted by experiment and described in book [12]; see also § 5, Ch. IX.

The presence of oxides, especially a small quantity of nitrogen peroxide, in heated air enveloped by the blast wave strongly affects the optical properties of the air in the wave, since, in distinction from molecules of oxygen and nitrogen, molecules of dioxide intensely absorb and radiate light in the visible part of the spectrum (NO molecules also do not absorb visible light).

Specific peculiarities of the kinetics of the chemical reactions of formation and disintegration of oxides of nitrogen in a blast wave

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*Molecular groups N_2O_4 do not absorb visible light, i.e., N_2O_4 gas is colorless. However, dioxide disappears after scattering of cloud of explosion in atmosphere, since the reaction $2NO_2 \rightarrow N_2O_4$ does not occur too fast.

lead to the appearance of interesting optical phenomena, observed during strong explosion, which also are described in book [12].

These phenomena — the glow of the shock wave at comparatively low temperatures after the front, of the order of 4000–2000° K, when gas, consisting only of molecules and atoms of oxygen and nitrogen, should not gleam; a rather sharp cessation of glow of shock wave at a temperature near 2000° K and a breaking away of the front of the wave from the boundary of the luminescent body, the so-called "fiery sphere"; the unique effect of the minimum of brightness of the fiery sphere at the time of breakaway, when the glow at first fades, and then the sphere, as it were, again inflames, — will be examined in §§ 5–7, Ch. IX. Here we will pause somewhat in greater detail on consideration of kinetics of reactions of oxidation of nitrogen in a blast wave, which is the necessary basis for the explanation of the shown optical phenomena. This problem was considered by one of the authors [13]. It is necessary to note that the study of kinetics presents an independent interest, as a characteristic example of an essentially nonequilibrium chemical process in the gas-dynamic phenomenon of a strong explosion.

Gas dynamics of a strong explosion were described in § 25, Ch. I. The process is self-simulating; the front of the shock wave spreads from the center of the explosion according to the law $R_f \sim t^{2/5}$. Distributions of all gas-dynamic magnitudes in radius are represented in Fig. 1.50. These distributions are constant in time in virtue of self-simulation; with the passage of time only scales change.

We are interested here in the course of chemical reaction in defined particles of air. For this, first of all, it is necessary to know how the thermodynamic state of a given particle changes with the passage of time.

On diagram r, t, Fig. 8.6, are schematically depicted lines of the front of the shock wave and several particles after the front, designated by figures 1, 2, 3. Heated and compressed at moments of passage of wave front t_{01}, t_{02}, t_{03}, particles are attracted by blast wave, while scattering from the center, and with this are adiabatically expanded and cooled until the pressure in them falls to atmospheric and particles stop.

Curves of expansion and cooling of air particles with the passage of time are schematically shown in Figs. 8.7 and 8.8.

Calculations by formulas in § 25 Ch. I show that during an explosion with energy $E = 10^{21}$ erg, to which will pertain all our numerical examples, the temperature in the front of the shock wave drops to magnitude $T_f = 2000°$ K during a period of the order of 10^{-2} sec from the moment of energy release. Of the same order are cooling times of air particles from a temperature of, let us say,

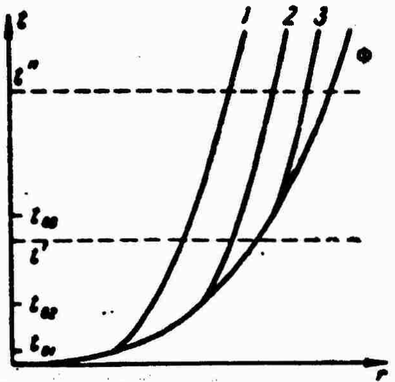

Fig. 8.6. r, t-diagram for a strong explosion in air. f) line of the front of the shock wave. 1, 2, 3) lines of three particles, through which the front passes at moments t_{01}, t_{02}, t_{03}.

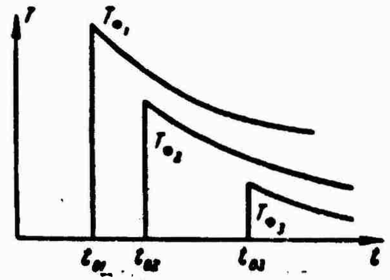

Fig. 8.7. Schematic dependence of temperature on time in three particles heated by blast wave.

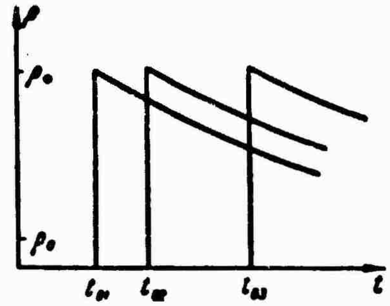

Fig. 8.8. Schematic dependence of density on time in three particles compressed by blast wave.

5000° K to 2000°–1500° K. Time $t \sim 10^{-2}$ sec is the time scale of the gas-dynamic process during an explosion with energy $E = 10^{21}$ erg, with which one should compare times characteristic for the course of chemical reactions.

Let us trace at first kinetics of reactions in any defined particle of air. Let us assume that, for instance, particle 1 was heated in the front of the shock wave to a temperature of $T_{f_1} =$ $= 3000°$ K. Speed of oxidation of nitrogen with such a temperature is very high and equilibrium concentration is attained during a period of the order of 10^{-6} sec. In a particle of air "instantly" approximately 5% of the nitrogen is oxidized and subsequently concentration of oxide "slowly" changes (decreases) in accordance with the laws of chemical equilibrium, while "following" cooling and expansion. Disintegration of oxide molecules starts to lag behind cooling only if the particles cool to a temperature of the order of 2300° K, at which relaxation time τ increases from initial small magnitude $\sim 10^{-6}$ sec to a magnitude comparable with gas-dynamic scale of cooling time, 10^{-2} sec. During further cooling, disintegration rapidly ceases, since the disintegration rate is very sharply lowered with decrease of temperature. Thus, already at 2000° K disintegration rate is characterized by a relaxation time $\tau \sim 1$ sec. The residual "hardened" quantity of oxide in a given particle corresponds approximately to that concentration which was in it at the time when relaxation time τ was comparable with characteristic time of cooling $t \sim 10^{-2}$ sec, i.e., when temperature in the particle was of the order of 2300° K. But slightly earlier the concentration was equilibrium, and equilibrium concentration rather weakly changes with decrease of temperature by several hundreds of degrees, which very essentially changes disintegration rate (see § 4 Ch. III and § 8 Ch. VI). Therefore, residual concentration of oxide in particles of air is simply equal to equilibrium concentration at a temperature near 2300° K, and this is a magnitude of the order of 1%. Dependence on time of the concentration oxide in a particle is schematically shown in Fig. 8.9. Certainly, the exact value of residual concentration depends on the specific particle, i.e., on the density with which it arrived at the abruptly changed (for reaction) temperature ≈2300° K, at which $\tau \sim t$, and on the time of cooling; however, these components do not affect the order of magnitude of the residual concentration. Reaction of the oxidation of oxide to dioxide at temperatures ~2000° K proceeds quite fast (see § 9, Ch. VI). Therefore, the concentration of dioxide still remains an equilibrium concentration, but dioxide is moreover in equilibrium, not with equilibrium but with an actual, "hardened" quantity of oxide. At temperatures of the order of 2000° K concentration of dioxide composes approximately 10^{-2}% (see Table 5.9, § 21 Ch. V). Subsequently all oxide gradually oxidizes to dioxide, where in the beginning this process "follows" after cooling, and then, at a temperature of ~1500° K and lower, lags behind cooling. Full oxidation of oxide occurs even in a quite cold particle, tens of seconds after the explosion.

In particles of air, which the front of the shock wave heats to a temperature below ~2200–2000° K, nitric oxide, in general, will not be formed since speed of oxidation with such a temperature is minute, and the particle fast skips that region of temperatures near 2000° K, in which the speed of the reaction composes still a noticeable magnitude. Thus, the spherical shell of air, heated in the front of the shock wave to a temperature of ~2200–2000° K, limits the mass of air in which, in general, oxide appears, and then dioxide (the law of motion of this layer is depicted on diagram r, t Fig. 8.6, let us say, by line 3). An estimate of the full quantity of nitric oxides which will be formed during a strong explosion follows from this. It is determined by the mass of air heated in front of the shock wave to a temperature higher than ~2200–2000° K and the equilibrium concentration of the oxide with such a temperature (at slightly higher – 2300° K), since namely with such temperatures there occurs hardening.* During an explosion with energy of 10^{21} erg the radius of the front of the shock wave, at a temperature of front $T_f = 2000°$ K, is equal to approximately 100 m. The mass of air in the spherical volume of such a radius composes approximately 5000 m and during concentration ~1% mass of oxide is found to be equal to ~50 m. The mass of dioxide, after connecting to every molecule of NO one more atom of oxygen, will compose ~75 m, i.e., nearly 100 m, as was mentioned above.

Let us consider now what the distribution is of the concentration of oxides in radius at a given moment of time. Here are possible two typical cases. If at considered moment t' (Fig. 8.10) temperature on the front of the wave is higher than ~2300° K, practically in all particles after the front concentrations of oxide and dioxide are equilibrium concentrations and distribution of

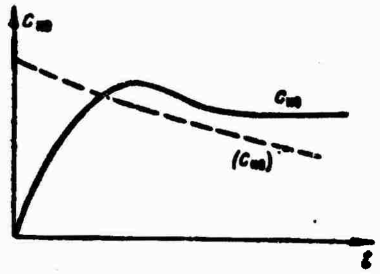

Fig. 8.9. Schematic dependence on time of equilibrium (C_{NO}) and actual (C_{NO}) concentrations of nitric oxide in a defined particle of air in the blast wave.

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*We remember that equilibrium concentration of nitric oxide in air depends only on temperature, not on density (see § 4 Ch. III and § 8 Ch. VI).

concentrations are determined simply by distributions of temperature and density after the front. An exception is only the very thin layer of air directly after the front, in which still by the given moment oxides have not been formed (Fig. 8.10).

If we concern ourselves with moment t'', at which the temperature behind the front is less than ~2000° K, for example 1600° K, then near the front there are found particles heated by the front up to a temperature lower than 2000° K; in them there are generally no oxides. Far behind the front, at a temperature higher than ~2500° K, the concentration in equilibrium, and in the intervening layer there are oxides, but their concentration is nonequilibrium. Close to the front it is less than the equilibrium concentration and a little further away, in those particles in which chilling has begun, it is higher [Fig. 8.11].

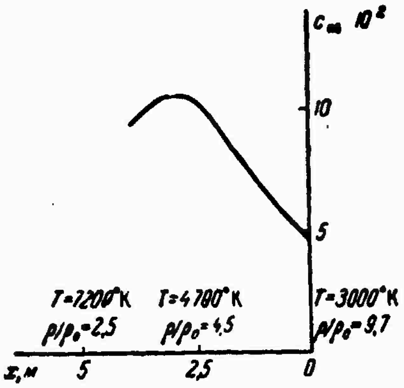

Fig. 8.10. Distribution of concentration of nitric oxide after the front of a shock wave during an explosion with energy

$E = 10^{21}$ erg

Temperature on front $T_f =$ $= 3000°K$. Concentration practically everywhere is equilibrium. Are shown value of temperatures and densities in several points.

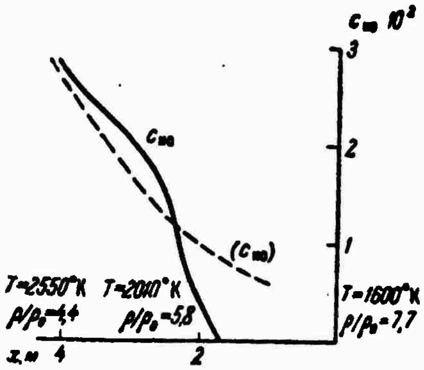

Fig. 8.11. Distribution of concentration of nitric oxide after the front of a shock wave during explosion with $E = 10^{21}$ erg. Temperature on the front $T_f =$ $= 1600°$ K. The solid curve is the actual concentration; the dotted one is equilibrium concentration. At $x > 4$m $c_{NO} \approx$ $\approx (c_{NO})$. There are shown values of temperatures and densities at several points.

For calculation of the concentration of oxide in a nonequilibrium region, and also for a more exact determination of quantity of "hardened" oxide, it is necessary to solve the equation of kinetics of oxidation reaction of nitrogen (6.45) in a given particle of air, taking into account the laws of its cooling and expansion in a blast wave. Laws of expansion and cooling of air, which follow from solution of problem about strong explosion (§ 25, Ch. I), it is possible to approximate fairly well by the following formulas, convenient for the calculation of kinetics:

$$\rho=\rho_0\left(\frac{t_0}{t}\right)^{2b},$$

$$\frac{1}{T}=\frac{1}{T_0}+\frac{a}{T_0}\ln\frac{t}{t_0},$$

where T_0 and ρ_0 are temperature and density in the particle at initial moment t_0, when through it passed the front of the shock wave; a and b are numerical constants depending only on effective adiabatic index in gas-dynamic solution. At $\gamma = 1.30$, $a = 0.44$, $b = 0.75$.

It turns out (see [13]) that by means of corresponding selection of new variables in the equation of kinetics (6.45) this equation, together with shown laws of cooling and expansion, it is possible to present in universal dimensionless form:

$$\frac{dy}{dx}=x^{2-\delta}(y^2-x^2), \tag{8.24}$$

where magnitude x is connected with a variable — time — and y is proportional to concentration of oxide; δ is a numerical constant less than unity. Initial condition, corresponding to absence of oxide at initial moment $t = t_0$, is reduced to condition $y = 0$, when x is equal to a certain magnitude of x_0, depending only on moment t_0, parameters of initial state and constants entering into equation of kinetics (6.45).

Ya. B. Zel'dovich, P. Ya. Sadovnikov, and D. A. Frank-Kamenetskiy [14] studied the kinetics of the oxidation reaction of nitrogen in laboratory conditions with a law of cooling of the type $\frac{1}{T} = \frac{1}{T_0} + \frac{a'}{T_0} t$ and constant density.

With this, the equation of kinetics (6.45), with the help of the introduction of new variables, also is reduced to an equation of the type (8.24) with initial condition $y = 0$ at $x = x_0$. In the book [14] solution of equation $y = y(x, x_0)$* is tabulated.

Knowing, from the gas-dynamic solution of the problem about strong explosion, parameters of initial state of a particle of air, it is possible thus to obtain a full solution, i.e., dependence of concentration of oxide c_{NO} on time. It fully corresponds to the qualitative considerations presented above. Thus, was calculated the curve depicted in Fig. 8.11.

3. Disturbance of Thermodynamic Equilibrium During Scattering of Gas in a Vacuum

§ 6. Scattering of a Gas Cloud

The phenomenon of scattering of a gas cloud into a vacuum is encountered in the most varied natural, laboratory, and technical processes. During impacts of meteorites against the surface of the planet there occurs a sharp braking of the meteorite and a transformation of kinetic energy into heat. If the speed of the blow is great, of an order of several tens of km./sec., there are developed very high temperatures of tens and hundreds of thousands of degrees.

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*As A. S. Kompaneyets noted, equation (8.24) with $\delta = 0$ is solved exactly, in Bessel functions.

The body of the meteorite and part of the ground of the planet are evaporated. The phenomenon reminds us of a strong explosion on the surface of the planet.* If the planet is without atmosphere, for instance as the Moon, the cloud being formed of steam, while possessing high rates of scattering, surmounts gravity force and is freely expanded into the vacuum. There exists an assumption that as a result of such "explosions" during blows of huge meteorites lunar craters were formed.

Analogous phenomena occur also during the much more frequent collisions of small bodies in the solar system — asteroids. Scattering into vacuum of colossal gas clouds is observed during flashes of Novae, when, as a result of the disturbance of energy balance of a star, there occurs an emanation of great energy; from the central layers to the periphery spreads a shock wave, detaching from the star and ejecting into outer space a gas cloud.

To a certain degree similar phenomena, but, of course, in incommensurably smaller scales, are encountered in laboratory conditions, for instance, during the evaporation of anode needles in pulse X-ray tubes under the action of powerful electron pulse (V. A. Tsukerman and M. A. Manakov [15]), during the explosion of wires by electrical current in evacuated installations, etc. Certainly, in laboratory conditions expansion is not infinite, since it is limited by the walls of the evacuated vessel; however, in the stage when the gas has still not reached the walls, scattering into vacuum occurs just as if vacuum were "infinite."

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*Hydro-dynamics of this process will be considered below, in Chapter XII.

Experiments, in which there is obtained a gas cloud scattering into a vacuum, were set up during rocket investigations of the upper layers of the atmosphere, when into space were released vapors of sodium and nitric oxide. The same phenomenon took place also during creation of artificial comet during flight to Moon of Soviet space rocket.

Dynamics of the scattering of a gas cloud into a vacuum is rather simple; an idealized problem about adiabatic scattering into vacuum of a gas sphere, when gas possesses constant heat capacity, was considered in §§ 28 and 29, Ch. I. Here we are interested in more delicate questions of the state of gas in a stage of large expansion, so to say, during scattering into infinity, which it is possible to consider on the basis of the most simple diagram of scattering. In this diagram is taken into account the behavior of only average in mass parameters of gas. It is clear that parameters of any specific particle of gas change in time exactly as average magnitudes, and differ from mean values only by numerical factors of the order of unity, which for us are immaterial.

Let us consider a gas sphere of mass M, possessing energy E.* In the stage of strong expansion almost all initial energy has already been turned into kinetic energy of scattering, and

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*We, for convenience, will remember here certain conclusions in § 28, Ch. I.

matter scatters inertially with average speed

$$u=\sqrt{\frac{2E}{M}}.$$

Radius of the sphere is of the order of R = ut; density of the gas drops with passage of time according to the law:

$$\rho=\frac{M}{4\pi R^3/3}=\rho_0\left(\frac{t_0}{t}\right)^3, \qquad (8.25)$$

where scale of time is approximately expressed through initial radius of sphere R_0 and density of substance ρ_0:

$$t_0=\left(\frac{M}{\rho_0\,4\pi u^3/3}\right)^{\frac{1}{3}}=\frac{R_0}{u}. \qquad (8.26)$$

If one were to be interested in temperature of gas in the stage of large expansion, then it is necessary to consider that small internal energy which still remains in the gas and which we disregarded during calculation of speed of scattering. Let us take into account that during adiabatic scattering there remains constant specific entropy of gas S. Considering for simplicity that matter behaves as gas with a certain constant effective value of adiabatic indes, we will obtain law of cooling of gas:

$$T=A(S)\,\rho^{\gamma-1}\sim t^{-3(\gamma-1)}, \qquad (8.27)$$

where A(S) is entropy constant, calculated by known formulas of statistical mechanics. If comparatively high temperatures are considered, then, taking into account processes of ionization, dissociation, etc., it is possible to assume tentative values of adiabatic index $\gamma \approx 1.2$–1.3. In any case the index is not larger than $5/3 = 1.66$, which corresponds to full freezing of all internal degrees of freedom of gas.

§ 7. The Effect of "Hardening"

We will observe how physical chemical processes take place in gas expanding by cubic law $\rho \sim t^{-3}$ and cooled according to the law $T \sim t^{-3(\gamma-1)}$.

We will assume that in the beginning the temperature was high, let us say, several tens or hundreds of thousands of degrees, so that molecules were dissociated and atoms strongly ionized. Let us assume also that initial density of gas also was great as this occurs if a gas cloud is formed as a result of fast energy release in initially solid matter. Then in the early stage of scattering with large density and temperature all relaxation processes occur very fast and gas is in thermodynamic equilibrium, where characteristics of its state, for instance degree of ionization or dissociation, "follow" after cooling and expansion. If the gas during all the scattering continued to remain in thermodynamic equilibrium, then as it expands and cools all electrons must be united with ions into neutral atoms, and all atoms possessing chemical affinity would be united into molecules.

Really, equilibrium degrees of ionization and dissociation depend on temperature by exponential law and on density only by power law: $\alpha_{\text{ioniz}} \sim \rho^{-1/2} \exp(-I/2kT)$, where I is ionization potential. During expansion ad infinitum and cooling to zero of temperature, equilibrium degrees of ionization and dissociation very fast rush to zero, since at $T \sim \rho^{\gamma-1} \rightarrow 0$ exponential member decreases much faster than increases pre-exponential factor. Being equilibrium, gas will scatter into infinity in the form of neutral molecules or atoms, if the latter do not possess chemical affinity, as, for instance, atoms of metals or inert gases (we now are distracted from the question of condensation of gas, which we will discuss subsequently).

It is easy to see, however, that however great speed of establishment of thermodynamic equilibrium might have been in the beginning, as compared to speeds of cooling and expansion, a moment must come when the relationship of the speeds of these processes will become inverse, thermodynamic equilibrium will cease to be established, and degree of ionization and dissociation will start to deviate from equilibrium values more and more.

Actually, during cooling, equilibrium shifts in the direction of a decrease in degrees of ionization and dissociation, i.e., recombination of electrons with ions and atoms into molecules predominates over ionization and dissociation. With high densities a basic role is played by recombination in triple collisions, and with low densities by photorecombination in paried collisions, so that by the stage of large expansion, interesting us, it is sufficient to estimate the speed of the latter.

Relaxation time for establishment of equilibrium ionization is of the order of $\tau \sim 1/n\bar{v}\sigma$, where n is the number of ions in 1 cm^3, proportional to density of gas; $\bar{v}$ is the thermal velocity of electrons, $\bar{v} \sim T^{1/2}$; and σ is effective section of photorecombination, which is inversely proportional to temperature $\sigma \sim T^{-1}$. Thus, owing to regularity (8.25), (8.27), relaxation time is proportional to

$$\tau \sim T^{\frac{1}{2}} \rho^{-1} \sim \rho^{\frac{\gamma-1}{2}-1} \sim t^{\frac{3}{2}(3-\gamma)}.$$

Even during the highest possible value $\gamma = 5/3$ magnitude of τ increases with passage of time as $\tau \sim t^2$. Characteristic time for noted changes of temperature and density is of the order of the actual moment t, since with power laws (8.25), (8.27)

$$\frac{dT}{dt} \sim -\frac{T}{t}, \quad \frac{d\varrho}{dt} \sim -\frac{\varrho}{t}.$$

Consequently, relaxation time grows faster than the gas-dynamic time scale and, starting from some moment, recombination will start all the more strongly and cooling will fall behind more strongly. Moreover, approximately from this moment the probability of recombination of a given electron with all ions during all the subsequent process of scattering, up to infinity, turns out to be less than unity, since the integral of probability of recombination or number of collisions converges.

Under the "hardest" conditions, when $\gamma = 5/3$ and $\tau = \tau_1(t/t_1)^2$, where t_1 is a certain arbitrary moment of time, and $\tau_1 = \tau(t_1)$, the number of acts of recombination of a given electron with ions for all time from t_1 and to ∞ is equal approximately to

$$w = \int_{t_1}^{\infty} n\bar{v}\sigma\, dt \approx \int_{t_1}^{\infty} \frac{dt}{\tau} \approx \int_{t_1}^{\infty} \frac{t_1^2\, dt}{\tau_1 t^2} \approx \frac{t_1}{\tau_1} = \text{const}. \tag{8.28}$$

Starting from moment t_1, at which relaxation time $\tau_1 > t_1$, the number of recombinations $w < 1$. Thus, during spherical scattering of gas into a vacuum equilibrium is not only disturbed, but recombination in general, does not proceed to the end. Gas, cooling temperatures to zero during scattering to infinity, remains partially ionized and dissociated: "hardening" of ions and atoms occurs.

Starting from a certain moment, in the gas are almost ceased gas kinetic collisions. Deactivation of vibrational and rotational excitation of molecules by impacts of particles is ceased. This follows from convergence of the same integral of collisions (8.28). However, hardening of molecular vibrations and rotations does not occur: vibrational and rotational energies of molecules pass due to spontaneous emission of light quanta. Vibrational transitions give radiation in the infrared region of spectrum, and rotational — in the radio range.

Regarding cases of nonspherical scattering, in principle during cylindrical symmetry of hardening, with respect to ionization, there exists ($n \sim t^{-2}$), and in flat cases it is lacking, since $n \sim t^{-1}$, and the integral of collisions with recombination $\int n\bar{v}\sigma dt \sim \int nT^{-1/2}dt \sim$ $\sim \int n^{2/3}dt \sim \int \frac{dt}{t^{2/3}}$ parts as $t^{1/3}$ at $t \rightarrow \infty$. Disturbance of ionization equilibrium, as will be shown in the following paragraph, occurs also in a flat case. Certainly, if we talk about a finite mass of gas, then during sufficiently large expansion "flat" (and "cylindrical") case certainly will cross into "spherical."

In view of the convergence of the integral of collisions with gas kinetic section placed in it, during spherical scattering with passage of time energy exchange of chaotic translational motion of atoms ceases. Further scattering continues in general, without collisions.*

All particles — atoms, ions, etc. — fly by inertia with speeds which they obtained as a result of the last collision. Besides particles, in general, possess a non-radial ("chaotic") component of

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*It is curious to note that "collisions" (more exactly, the interaction of particles) do not cease in the case of scattering of completely ionized gas, since effective section of "collisions" is $\sigma \sim$ $\sim T^{-2}$ and at $\gamma = 5/3$, $T \sim n^{2/3}$ the integral of collisions parts even in a spherical case: $\int n\bar{v}\sigma\, dt \sim \int nT^{1/2}T^{-2}dt \sim \int dt \rightarrow \infty$. The expansion into vacuum of a gas cloud without collisions (in approximation of free molecular flux) is examined in the work of Molumd [15a]. See also [24, 25].

speed. One would think, "hardening" of chaotic speed should occur, i.e., "temperature." In reality there is none, for reasons of purely geometric character. The question consists of the definition of the ideas of "hydrodynamic" and "internal" energies in conditions of the absence of collisions of particles. As V. A. Belokon' [16] noted, the internal energy of a unit of volume of gas is equal to the difference between full kinetic energy $n\frac{m\overline{v^2}}{2}$ (n in the number of particles in 1 cm^3, m is their mass, and $\overline{v^2}$ is mean square of speed) and kinetic energy of "hydrodynamic" motion $n \times \frac{m(\overline{v})^2}{2}(\overline{v})^2$ is square of mean speed):

$$E_{\text{внутр}}=E_{\text{полн}}-E_{\text{гидрод}}=n\frac{m}{2}(\overline{v^2}-(\overline{v})^2).$$

Let us assume that collisions cease at the time t_1 when gas occupies a sphere of radius r_1 (Fig. 8.12). At points A and B particles arrive from this sphere at moments t' and t'', possessing speeds whose directions are included in cones shown in Fig. 8.12.

It is clear that the more the distance from center, the less the flare of the cone and the nearer $\overline{v^2}$ to $(\overline{v})^2$, i.e., the less difference $\overline{v^2} - (\overline{v})^2$. In limit $t \to \infty$, $r \to \infty$ all particles fly in a strictly radial direction and $\overline{v^2} = (\overline{v})^2$, i.e., all kinetic energy is turned into "hydrodynamic."

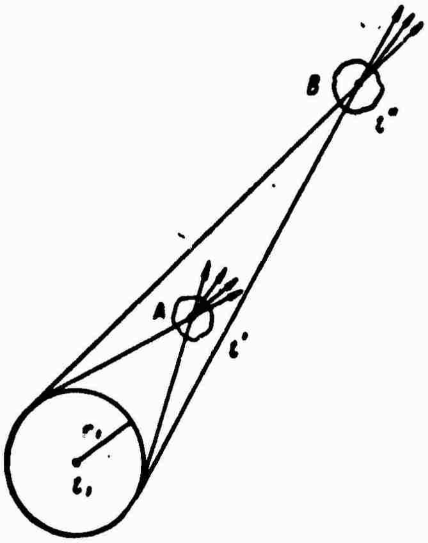

Fig. 8.12. Concerning the question of scattering of gas into a vacuum without collisions.

§ 8. Residual Ionization

Let us consider kinetics of ionization and recombination during scattering of gas into a vacuum and we will estimate residual ionization in gas during its expansion ad infinitum (results expounded below were obtained in the work of one of the authors [17]). Let us assume that in the beginning temperature of gas was high and atoms were repeatedly ionized. During adiabatic cooling of expanded gas degree of ionization decreases, electrons "sit in their own places" in atoms. We will consider scattering that is not too fast, when recombination of electrons with repeatedly ionized atoms in early stage of scattering proceeds so fast that at each moment there is ionization equilibrium. We will consider that ionization equilibrium is disturbed only in that stage, when the last electrons "sit in their own places," i.e., when a process reverse to first ionization takes place.

Let us compose an equation of kinetics in the region of first ionization, taking into account two basic mechanisms: ionization by electron impact and photo-ionization and the corresponding inverse processes of recombination. Ionization by heavy particles, which is essential only during extraordinarily small concentrations of free electrons, it is possible to disregard. Equations of kinetics (6.70) and (6.91) it is somewhat convenient to convert, expressing members of ionization through coefficients of recombination with the help of the principle of detailed equilibrium by the formulas (6.71), (6.72), and (6.92). Introducing, instead of numbers of ions and electrons in 1 cm^3 $N_+ = N_e$, the degree of ionization $x = N_e/N$, where N is the number of initial atoms in 1 cm^3, and considering that degree of ionization is small, $x << 1$, we will record the equation of kinetics in the form

$$\frac{dx}{dt} = bN(x_p^2 - x^2). \qquad (8.29)$$

Here x_p is equilibrium (at given temperature and density) degree of ionization, which is expressed by Saha formula. At $x_p << 1$ formula

(6.72) gives

$$x_p = 6{,}96 \cdot 10^7 \left(\frac{g_+}{g_a} \frac{T^{\circ \frac{3}{2}}}{N} \right)^{\frac{1}{2}} e^{-\frac{I}{2kT}}, \tag{8.30}$$

b is total coefficient of recombination; by the formulas (6.77), (6.94), it is equal to

$$b = b_v + b_e = \bar{v}_e \sigma_c + 1{,}28 \cdot 10^{-10} \frac{g_a}{g_+} \left(\frac{I}{kT} + 2 \right) \frac{\sigma_e N x}{T^\circ}. \tag{8.31}$$

During known laws of expansion and cooling N(t), T(t), which are given by formulas (8.25) and (8.27), expression (8.29) constitutes an ordinary differential equation relative to sought function x(t). Inasmuch as we are interested mainly in the qualitative side of the matter, we will solve this equation approximately.

At first speeds of ionization and recombinations, proportional to both components in the right part of equation (8.29), are great as compared to speeds of expansion and cooling. (For comparison of speeds of different processes we consider relative speeds, measured in reverse seconds, for instance, $\frac{1}{T}\frac{dT}{dt}$, $\frac{1}{N}\frac{dN}{dt}$.) Ionization and recombination almost completely compensate one another; degree of ionization "follows" after expansion and cooling, remaining close to equilibrium. Approximately $x(t) \approx x_p(t) \equiv x_p[T(t), N(t)]$ and difference $|x_p^2 - x^2| \ll x_p^2$.

The small deviation of the degree of ionization from equilibrium, which inevitably exists, inasmuch as temperature and density change in time, it is possible to estimate approximately, considering in the left part of equation (8.29) $dx/dt \approx dx_p/dt$, replacing x in expression for coefficient of recombination (8.31) by x_p, and also considering $x_p^2 - x^2 \approx 2x_p(x_p - x)$. It is easy to see that relative deviation $|x_p - x|/x_p$ grows with passage of time (since speed of relaxation process becomes less and less as compared to speed of change of macroscopic parameters — temperature and density).

Ionization equilibrium noticeably is disturbed and starts hardening when difference of speeds of ionization and recombination increases to a magnitude of the order of the speeds themselves, i.e., when magnitude $|x_p^2 - x^2|$ becomes of the order of x_p^2.

It is possible to estimate the moment of "beginning of hardening" t_1 and magnitudes T_1, N_1, x_1, at this instant, considering, as earlier, $dx/dt \approx dx_p/dt$, $x \approx x_p$ in coefficient of recombination and equating difference $x^2 - x_p^2$ magnitude x_p^2.

Differentiating with respect to time the equilibrium degree of ionization by the formula (8.30), taking into account the fact that the exponential Boltzmann factor changes the fastest of all, and using law of cooling (8.27), which gives $\frac{dT}{dt} = -3(\gamma - 1)\frac{T}{t}$, we will find the equation determining the moment of "beginning of hardening":

$$b_1 N_1 x_{p1} t_1 = \frac{3}{2}(\gamma - 1)\frac{I}{kT_1}. \qquad (8.32)$$

Here $b_1 = b(T_1 N_1 x_{p1})$. This equation, jointly with expressions for laws of expansion and cooling (8.25), (8.27), and Saha formula (8.30) referred to moment t_1, is reduced to transcendental equation for temperature T_1. Finding T_1, it is easy to calculate the remaining magnitudes t_1, N_1, and x_{p1}. (In given approximation the actual degree of ionization x_1 it is possible to consider equal to equilibrium x_{p1}.)

After "beginning of hardening" speed of ionization, proportional to x_p^2, continues rapidly to decrease with passage of time by exponential law $e^{-\frac{I}{kT(t)}}$. Recombination rate, proportional to square of actual degree of ionization, in virtue of hardening, drops much slower and soon becomes considerably higher than speed of ionization: $x(t) \gg x_p(t)$. In these conditions, acts of ionization it is possible to disregard, assuming that only recombination occurs. Equation of kinetics is then written approximately in the form

$$\frac{dx}{dt} = -bNx^2 \text{ at } t > t_1.$$

This differential equation is reduced to quadrature, if we disregard two as compared to I/kT in coefficient of triple recombination, which always can be done, and put approximately adiabatic index $\gamma = 5/3$. With such particular value of adiabatic index both members of recombination turn out to be equally time-dependent owing to equation of adiabat $T \sim N^{2/3} \sim t^{-2}$ and from both members it is possible to take time factor t. The equation is reduced to quadrature, and during an arbitrary value of adiabatic index, if one of the two mechanisms of recombination predominates, it is possible to disregard the second. In this last case the final expressions turn out to be especially simple. Inasmuch as dependence of the solution on index γ in a reasonable interval of values of γ from $\gamma \approx 1.3$ to $\gamma \approx 5/3$ is not too strong, we will write out final expressions for $\gamma \approx 5/3$.

If gas is expanded fast, hardening starts early, during high density and degree of ionization. Recombination occurs mainly in three-body collisions and residual ionization, corresponding to $t \to \infty$, is equal to $x_\infty = x_1(kT_1/2I)^{1/2}$.

If, however, gas is expanded slowly, hardening starts late, in a stage of strong scattering and cooling, during small concentration of electrons. Electrons recombine with ions basically in double collisions with the emission of light quanta. Residual degree of ionization in this case is equal to $x_\infty = x_1(kT_1/I)$.

Let us note that in this (the last one) case the gas sphere turns out to be, as a rule, transparent for quanta emitted during photorecombination. Quanta desert the sphere, removing with themselves ionizing energy, which, consequently, does not participate in acceleration of gas. Into kinetic energy of scattering at this stage passes only energy of translational degrees of freedom of particles if gas is monatomic, so that the adiabatic index in this case is indeed close to 5/3.

For example we will estimate residual ionization of gas from atoms of iron, forming during fast heating and evaporation of metallic iron. Let us assume that initial heating during normal density of solid iron corresponds to temperature $T_0 = 116{,}000^\circ$ K = 10 ev. Appraisal of initial energy and entropy, taking into account electronic specific heat (according to method in § 14 Ch. III), gives $\varepsilon_0 = 72$ ev/atom, S = 61 cal/mole degree. Speed of scattering with this is u = 15.5 km/sec.

If initial radius of sphere is $R_0 = 10$ m (large iron meteorite), then at the time of beginning of hardening during scattering up to a radius of $R_1 = 800$ m $T_1 = 4550^\circ$ K, $N_1 = 1.4 \cdot 10^{17}$ cm^{-3}, $x_1 = 4.2 \cdot 10^{-3}$ and residual ionization $x_\infty = 2.1 \cdot 10^{-4}$.

If initial radius is $R_0 = 1$ cm, which is close to laboratory scales, then $R_1 = 50$ cm, $T_1 = 9300^\circ$ K, $N_1 = 6.6 \cdot 10^{17}$ cm^{-3}, $x_1 = 0.58$ and $x_\infty = 0.13$. Residual ionization is the greater, the relatively faster expansion and cooling occurs, i.e., the smaller the mass of the gas sphere and the higher the initial heating.

§ 9. Remarks About Flat Scattering and About Expiration of Gas into a Vacuum

During scattering of a flat layer residual ionization is equal to zero, although ionization equilibrium is essentially disturbed and degree of ionization aspires to zero not by exponential law, as equilibrium, but much slower, by power law. Really, taking into account only one photo-recombination, which always becomes predominant during sufficiently strong expansion, we will find

$$\frac{dx}{dt} = -bNx^2 = -\bar{v}_e\sigma_e N x^2 \sim -\frac{Nx^2}{T^{\frac{1}{2}}}.$$

At $\gamma = 5/3$ $T \sim N^{2/3}$. In a flat case $N \sim t^{-1}$, $T \sim t^{-2/3}$, so that $dx/dt \sim -x^2/t^{2/3}$. Integrating, we will obtain $\frac{1}{x} - \frac{1}{x_1} \sim t^{1/3} - t_1^{1/3}$.

At $t \to \infty$ degree of ionization aspires to zero, as $x \sim t^{-1/3} \to 0$, i.e., by power law, whereas equilibrium degree of ionization aspires to zero by exponential:

$$x_p \sim \exp\left(-\frac{I}{2kT}\right) \sim \exp\left(-\mathrm{const}\, t^{\frac{2}{3}}\right).$$

Disturbance of ionization equilibrium, similar to that which occurs during scattering into vacuum of a flat layer, takes place even on the edge of a wave of rarefaction, during flat expiration of gas into a vacuum (see § 11 Ch. I). Let us assume that wave of rarefaction is propagated along motionless gas with initial density and speed of sound ρ_0, c_0. During expiration into a vacuum the front boundary of the gas flies with speed $u_1 = -\frac{2c_0}{\gamma - 1}$ (see Fig. 8.13). Head of wave of rarefaction spreads along initial gas with speed of sound c_0. It is easy to show that density of assigned particle of gas with Lagrange coordinate m g/cm^2, calculated from boundary with vacuum, with passage of time drops according to the law:

$$\rho = \rho_0 \left(\frac{m}{\rho_0 c_0 t}\right)^{\frac{2}{(\gamma+1)}} \sim t^{-\frac{2}{\gamma+1}} \text{*)},$$

---

*If x_1 is a coordinate of the boundary of gas $x_1 = u_1 t = -\frac{2}{\gamma - 1} c_0 t$, then from formulas (1.54), (1.55), (1.56) § 11 Ch. I it follows that at time t density is distributed on coordinate x according to law:

$$\rho = \rho_0 \left\{\left[\frac{(\gamma-1)}{(\gamma+1)}\right]\left[\frac{(x-x_1)}{c_0 t}\right]\right\}^{\frac{2}{\gamma-1}}.$$

Lagrange coordinate of a particle of gas, which is at time t at point x, is equal to

$$m = \int_{x_1}^{x} \rho\, dx = \rho_0 \left[\left(\frac{\gamma-1}{\gamma+1}\right)\right]^{\frac{\gamma+1}{\gamma-1}} (c_0 t)^{-\frac{2}{\gamma-1}} (x-x_1)^{\frac{\gamma+1}{\gamma-1}}.$$

Expressing $x - x_1$ through density ρ, we will find

Footnote continued on following page

i.e., somewhat more slowly than during scattering of flat layer into vacuum (for instance, at $\gamma = 5/3$, $\rho \sim t^{-3/4}$).

With this, hardening is lacking, but thermodynamic equilibrium is disturbed just as in the case of scattering of a flat layer when $\rho \sim t^{-1}$: degree of ionization aspires to zero with passage of time by power law (certainly, with another exponent), but not by exponential law.

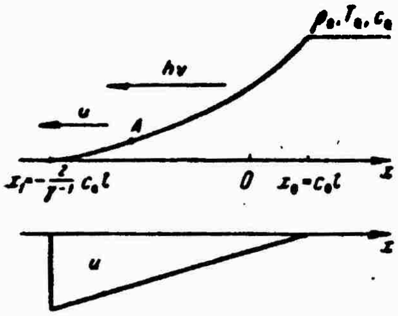

Fig. 8.13. Concerning the question about expiration of gas into a vacuum.

It is interesting to note that in this case, when we are interested in magnitudes not averaged with respect to the entire mass of gas but pertaining to a certain gas particle, actual "equilibrium," more exactly, "stationary" value of ionization differs from the thermodynamically equilibrium value. Actually, the particle is in the field of radiation, which goes from deeper layers where temperature is higher. "Stationary" degree of ionization corresponds to an equality of numbers of ionizations and recombinations in 1 cm^3 in 1 sec. But photo-recombination does not depend on density of radiation (induced recombination is immaterial), and photo-ionization proceeds more intensely than in the case when density of radiation corresponds to temperature of the actual particle. In the particle is bias lighting from without, reignition from an outside source — radiation, proceeding from high-temperature layers (Fig. 8.13). Therefore, even the "stationary" level of ionization should be higher than this follows from the laws of thermodynamic equilibrium.

FOOTNOTE CONTINUED FROM PRECEDING PAGE

$$m = \rho_0 c_0 t \left(\frac{\rho}{\rho_0}\right)^{\frac{\gamma+1}{2}},$$

whence follows given formula.

4. Condensation of Vapor During Adiabatic Expansion

§ 10. Saturation of Vapor and Appearance of Centers of Condensation

If the vapor of any substance is adiabatically expanded and cooled, then it, at a certain moment, becomes saturated and then supersaturated, after which condensation starts. It is known that condensation is strongly facilitated in the presence of ions, dust motes, alien particles, which become centers of condensation and around which are formed drops of liquid. Ions and dust motes create even more favorable conditions for the fastest formation of centers of condensation, but their presence is not at all obligatory. In pure supersaturated vapor, centers of condensation appear as a result of the adhesion of molecules into molecular complexes. After the achievement of so-called critical sizes complexes become stable, do not disintegrate and reveal a tendency toward further growth and transformation into drops of liquid.

The phenomenon of condensation of vapor during adiabatic expansion is encountered in technology, in the laboratory, and in nature. It lies in the basis of the work of a cloud chamber, widely used in nuclear physics for registration of fast charged particles. A cloud chamber is a vessel filled by vapors of water, alcohol, or other liquids. The needed supersaturation is created thanks to the expansion of vapor during fast movement of a piston. Vapor is condensed on ions, which are formed along the trajectory of a fast particle, and drops of liquid are registered by optical methods.

Condensation of water vapor contained in air frequently is observed during the expansion of air in wind tunnels. Condensation of water vapor contained in atmosphere and gases passing from the jets of jet engines leads to the formation of a characteristic trace during the motion of jet aircraft.

The fact that during adiabatic expansion of vapor at a certain moment condensation should start is easy to explain with the help of a temperature — specific volume diagram. As is known from thermodynamics, the pressure of saturated vapor, being in equilibrium with liquid, obeys the equation of Clapeyron — Clausius (see, for instance, [18]). If it is possible to consider vapor as ideal gas, then this equation leads to the following connection between specific volume of saturated vapor V_{vap} and temperature*:

$$V_{\text{пар}} = BTe^{\frac{U}{RT}}, \quad T = \frac{U}{R}\left(\ln\frac{V_{\text{пар}}}{BT}\right)^{-1}, \qquad (8.33)$$

where U is heat of evaporation, R is gas constant, and B is coefficient which it is possible to consider approximately constant.

From this formula it is clear that temperature of saturation depends on volume of vapor very weakly, by logarithmic law. On the other hand, adiabat of Poisson for vapor constitutes a curve of exponential type $T \sim V^{-(\gamma-1)}$, which must intersect curve of saturation (Fig. 8.14). At the point of intersection O, earlier unsaturated expanded vapor becomes saturated.

Let us trace movement of process in time. If vapor is always expanded, then specific volume monotonically grows with the passage of time. Instead of considering change of temperature in time T(t), it is possible to consider change of temperature with increase of volume $T(V) = T[V(t)]$, using diagram T(V) (see Fig. 8.14).

Crossing into state of saturation, vapor continues to be expanded, following adiabat of Poisson, and becomes supersaturated

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*This follows from formulas $p = \text{const}\ e^{-\frac{U}{RT}}$, $pV = RT$, where p is pressure of saturated vapor.

(supercooled). Speed of formation of centers of condensation very sharply depends on degree of supersaturation. Therefore, during further increase of degree of supersaturation the number of nuclei of liquid phase fast increases. Soon after passage of the state of saturation the speed of condensation attains such a magnitude that emanation of latent heat stops the growth of supersaturation (if, of course, expansion occurs not too fast).

Condensation is accelerated even during a constant number of centers due to increase of surface of drops, to which adhere molecules of vapor. Accelerated condensation not only stops growth of supersaturation but leads even to a decrease in degree of supersaturation. Formation of new nuclei, which, in the highest degree, is sensitive to the magnitude of supersaturation, immediately ceases and subsequently condensation proceeds by means of the adhesion of molecules to drops already available. Thus, all centers of condensation, as a rule, are engendered in the actual beginning of the process of condensation, as soon as there is attained a sufficiently large supersaturation.

During work with a cloud chamber vapor is quickly expanded to a defined volume so that in it is created known initial supersaturation. This supersaturation is chosen so large that all ions became centers of condensation and by the number of drops it is possible to count number of ions.* Thus, a question about the number of centers of condensation does not appear here.

It is another matter in gas-dynamic processes, such as expansion of gas in wind tunnels, expiration from jets, or the scattering of a gas cloud formed as a result of heating and evaporation of initially solid matter, for instance metal. Here speed of expansion

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*At the same time nuclei not containing ions virtually are not formed.

is determined by the general dynamics of the process, and the number of centers of condensation, i.e., in the end the number of drops of condensate, is unknown and depends on speed of expansion. Even if in the gas there are ions (which does not always occur, of course), during sufficiently slow expansion they do not all become centers of condensation by far. In virtue of the above-stated causes, supersaturation in the system due to intensely proceeding condensation can fall after only part of the ions are turned into centers of condensation. All the more unknown is the number of centers in pure vapor in the absence of outside particles. The number of centers of condensation depends on the maximum accessible supersaturation (supercooling) and is determined by the play of opposite influences: cooling of vapor owing to the accomplishment of the work of expansion and the heating of it due to emanation of latent heat during condensation.

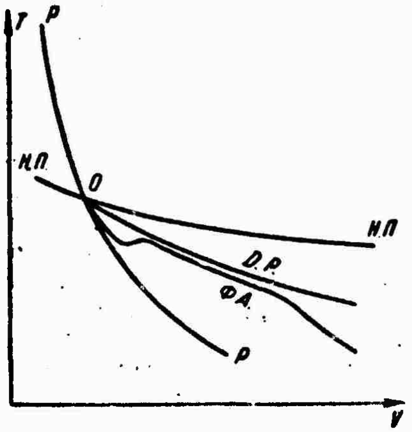

Fig. 8.14. T, V-diagram for condensation process during adiabatic expansion of vapor. P) adiabat of Poisson for vapor; NP) curve of saturated vapor; O) point of saturation; DR) adiabat of an equilibrium, two-phase, vapor-liquid system; FA) actual adiabat of vapor-liquid drops system, taking into account kinetics of condensation.

In § 12 it will be shown how it is possible to calculate number of centers of condensation, knowing speed of expansion and cooling of vapor.

§ 11. Thermodynamics and Kinetics of the Condensation Process

Let us consider the process of condensation in an adiabatically expanded substance from a purely thermodynamic point of view, i.e., assuming that at every moment of time there is thermodynamic equilibrium. Up to the moment of saturation vapor was expanded, following adiabat of Poisson. After achievement of a state of saturation and the beginning of condensation, substance constitutes already a two-phase vapor-liquid system, and equation of adiabat is complicated both due to transformation of part of gas phase into liquid with different thermodynamic properties and because of emanation of latent heat. Equation of adiabat of a two-phase system it is possible to record in the following form:

$$[c_1(1-x)+c_2x]\,dT+RT(1-x)\frac{dV}{V}-[U-(c_2-c_1)T]\,dx=0. \qquad (8.34)$$

Here c_1 is heat capacity of vapor during constant volume; c_2 is heat capacity of liquid; x is degree of condensation, defined as the ratio of the number of molecules in liquid phase to the total number of molecules in a given mass of matter; V is specific volume of matter, which is less than specific volume of vapor with respect to 1 - - x: $V = V_{vap}(1 - x)$.* In this equation we disregarded surface energy of drops of liquid, which is very small as compared to latent heat, if drops contain many molecules. Equation of adiabat (8.34) is accurate even in the absence of thermodynamic equilibrium. If the state is nonequilibrium, the degree of condensation x is determined by kinetics of condensation. In conditions of thermodynamic equilibrium, i.e., "infinitely" slow expansion, vapor at each moment is in equilibrium with liquid, i.e., is saturated. The state of matter changes along curve of saturation (8.33), which, if one were to

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*Specific volume of two-phase system $V = V_{liq}x + V_{vap}(1 - x)$, where V_{liq} is specific volume of liquid phase. Inasmuch as density of liquid is much higher than vapor density, at a degree of condensation not too close to unity, the first member it is possible to disregard: $V \approx V_{vap}(1 - x)$. Heat capacities of liquid and vapor c_2, c_1 in formula (8.34) are assumed constant.

replace specific volume of vapor by specific volume of matter, obtains the form

$$\frac{V}{1-x}=BTe^{\frac{U}{RT}}. \tag{8.35}$$

If we exclude from the two equations (8.34) and (8.35) degree of condensation x, we will obtain a differential equation, which describes the adiabatic process in a two-phase system in variables T, V. Solution of this equation gives adiabat T(V). Constant of integration in the common solution is determined by entropy of matter. It is possible to express by temperature and volume at point of saturation O, since adiabat, obviously, passes through this point. We will not here write out the solution but will depict adiabat in Fig. 8.14. It is spread somewhat lower than the curve of saturation, which is clear from comparison of formulas (8.33) and (8.35), if one were to consider that x > 0.1 - x < 1. During small degree of condensation, when x << 1, adiabat of a two-phase system almost coincides with curve of saturation. Divergence of both curves determines degree of condensation x:

$$1-x=\frac{V(T)}{V_{\text{пар}}(T)}.$$

Degree of condensation monotonically increases along adiabat with increase of volume.

It is curious to note that during adiabatic expansion of matter ad infinitum, V → ∞ (and cooling to zero of temperature, T → 0), degree of condensation along a thermodynamically equilibrium adiabat aspires to unity: x → 1.

In other words, during unlimited expansion of matter, according to the laws of thermodynamics vapor should be completely condensed. During adiabatic expansion to a defined volume is condensed only a defined part of vapor.

In reality, of course, the state of matter in the process of condensation never can exactly follow equilibrium adiabat; it only more or less nears equilibrium, with which the nearer to equilibrium the more slowly external conditions change, i.e., the more slowly expansion occurs.

Above it has already been noted that centers of condensation are engendered basically immediately after the passage of the state of saturation, at the time of achievement of maximum supersaturation. After that, if only expansion does not occur too fast, accelerated condensation restricts growth of supersaturation and new nuclei do not appear. The state of matter passing through maximum deviation from equilibrium adiabat (D. R.) (Fig. 8.14, maximum supercooling), nears equilibrium.

However, degree of supercooling does not drop to zero and actual adiabat (F. A.) never attains thermodynamic equilibrium (D. R.), passing always lower than the latter. Condensation now proceeds because of growth of drops. Simultaneously two processes occur: direct — the adhesion of molecules of vapor to drops — and the reverse — the evaporation of drops. Speed of growth of drops (i.e., speed of condensation) is determined by the difference in speeds of direct and inverse processes, with which the greater it is the higher the degree of supersaturation. In saturated vapor, i.e., on equilibrium adiabat, adhesion and evaporation accurately compensate one another and growth of drops is lacking.*

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*A thermodynamically equilibrium adiabat, strictly speaking, corresponds to the state of saturation with respect to a flat surface of liquid, i.e., with respect to drops of "infinitely large" radius.

In the course of condensation degree of supersaturation, regulating the balance between adhesion and evaporation, automatically is adjusted to the process in such a way that there exists a surplus of adhesion over evaporation and that speed of condensation "follows" after expansion of substance. In the system is maintained a state close to equilibrium, i.e., to saturation.

Considerable deflection from thermodynamic equilibrium can occur only during very strong expansion, when acts of adhesion become too rare.

Thus, during the scattering of vapor into a vacuum, the speed of adhesion, which is proportional to vapor density, i.e., t^{-3}, from a certain moment is no longer in a state to follow expansion; condensation ceases, and the remainder of the vapor scatters to infinity, again following Poisson's adiabat of gas (Fig. 8.14). There occurs hardening, i.e., into infinity matter scatters, not completely condensed as the laws of thermodynamics require but partially in the form of gas and partially in the form of drops of condensate (for greater detail about this see the following paragraph).

During fast expansion of matter, condensation cannot "follow" expansion, and from the very beginning the state considerably deviates from thermodynamic equilibrium. During very fast expansion to a defined volume, as takes place in a cloud chamber, condensation cannot occur during the time of expansion and starts only after expansion ceases. During very fast expansion into a vacuum, condensation does not occur at all and matter scatters into infinity in the gas phase. This corresponds to the biggest deflection from thermodynamic equilibrium and maximum hardening.

§ 12. Condensation in a Cloud of Evaporated Matter, Scattering into a Vacuum

In this paragraph more specifically is considered the process of condensation during the expansion of vapor; there will appear basic ways of quantitative calculation, and numerical results are presented. Let us observe how condensation proceeds in a cloud of evaporated matter expanding into a vacuum. We will consider the phenomenon of "explosion" of large meteorites during an impact against the surface of a planet (deprived of atmosphere) or during collisions with asteroids, about which was mentioned in the beginning of § 6. We are interested in the question, in what form does evaporated matter of the ground of a planet and the body of a meteorite scatter into interplanetary space: in the form of pure gas or in the form of ultimate particles and what are the dimensions of the latter? The solution of this problem was obtained in the work of one of the authors [19].*

All numerical results will refer to the condensation of the vapor of iron, in reference to the case of the evaporation of the body of iron meteorites. Let us observe when a state of saturation is attained during expansion of iron vapor. Below, in the table, are represented calculated temperature T_1 and density (number of atoms in 1 cm^3 n_1) of vapor at the time of saturation for several values of entropy of vapor S. Assuming that the process of expansion proceeds adiabatically, it is possible to say that the very same entropy is possessed by "solid" iron at the time of heating. In the table are represented magnitudes of initial heating ε_0 and temperature T_0 of iron during normal density of solid metal, corresponding to these

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*Certain qualitative remarks about the phenomenon of condensation of an evaporated substance were done in the work of the authors [20].

values of entropy. These magnitudes were calculated with the help of the method presented in § 14, Ch. III (considered are both the nuclear and the electron part of heat capacity). In the last column stand the average speeds of scattering of a gas sphere of iron atoms, estimated by the formula $u = \sqrt{2\varepsilon_0}$ (see § 6), i.e., on the assumption that by the moment of condensation, vapor was already strongly cooled and all initial energy of heating was turned into kinetic energy of scattering.

Let us estimate the number of centers of condensation, i.e., number of particles of condensate in final state. The theory of formation of nuclei of liquid phase in pure supersaturated vapor was well-developed by a number of authors: Fol'mer, Bering, and Dering, Farkash, Ya. B. Zel'dovich, Ya. I. Frenkel'. A detailed account of it with references to original works can be found in a book of Ya. I. Frenkel' [21] (see also [22]). We will remember here only basic positions of this theory.

ε_0, $\frac{\text{ev}}{\text{atom}}$	T_0, ev	S, $\frac{\text{cal}}{\text{mole}\cdot\text{deg}}$	$T_1^{\bullet}$, °K	n_1, $\frac{1}{\text{cm}^3}$	u, $\frac{\text{km}}{\text{sec}}$
25,6	5	48,3	3100	$8{,}01 \cdot 10^{19}$	9,2
71,9	10	60,8	2130	$7{,}15 \cdot 10^{16}$	15,5
138	15	71,5	1700	$2{,}86 \cdot 10^{14}$	21,4
222	20	81,3	1430	$1{,}43 \cdot 10^{12}$	27,2

In vapor phase, from time to time, occur fluctuations, at which molecules of vapor cohere, forming molecular complexes – nuclei of liquid phase. In unsaturated vapor, when gas phase is stable, complexes are unstable and soon disintegrate (are evaporated). In supersaturated vapor only complexes of very small dimensions are unstable. Increase of the smallest complexes because of adhesion of new molecules is unprofitable with respect to power because of growth of surface energy on the boundary between liquid and gas phases. Growth of complexes of sufficiently large dimensions is profitable with respect to power since favorable volume energy effect (emanation of latent heat) during sufficiently large dimensions becomes larger than unfavorable surface. During every degree of supersaturation there exist defined, critical sizes of complexes. Supercritical nuclei (with radius larger than critical) are stable, "viable" and reveal a tendency toward further growth and transformation into drops of liquid. Speed of formation of viable nuclei of centers of condensation is proportional to the probability of the appearance of complexes of critical sizes. For the formation of such complexes there should be expended some energy $\Delta\Phi_{max}$; it is necessary to surmount the potential barrier, therefore, the probability of such fluctuations, according to the law of Boltzmann, is proportional to exp $(-\Delta\Phi_{max}/kT)$.

Magnitude of potential barrier $\Delta\Phi_{max}$ or activation energy depends on critical radius of the complex and is simply connected with the degree of supersaturation, which it is possible to characterize, for instance, as a magnitude of supercooling

$$\theta = \frac{T_p - T}{T_p}.$$

Here T_p is vapor temperature, saturated at a given density, and T is actual vapor temperature.

Speed of formation of viable nuclei, i.e., the number of centers of condensation from calculation per one molecule of vapor, appearing in 1 sec. in stationary conditions, when in the system there is maintained constant supersaturation (supercooling), and supercritical nuclei depart from the system with replacement by an equivalent quantity of vapor, is equal to

$$I = Ce^{-\frac{b}{\theta^2}}, \qquad (8.36)$$

where

$$C = n\bar{v}2\omega\sqrt{\frac{\sigma}{kT}},$$

$$b = \frac{16\pi\sigma^3\omega^2}{3k^3q^2T}.$$

Here n is the number of molecules of vapor in 1 cm^3; $\bar{v}$ is their thermal velocity; σ is surface tension; ω is volume in liquid, happening per one molecule; q = U/R is expressed in degrees of heat of evaporation. Critical radius r* of a nuclei is connected with degree of supercooling by the formula

$$\theta = \frac{2\sigma\omega}{kqr^*}.$$

It is possible to generalize a theory in the case of electrically charged nuclei inside which is an ion (see [19]). Speed of formation of nuclei, as before, is described by formula (8.36); only constant b decreases.

Let us compose an equation of the kinetics of condensation. Let us make a basic assumption about the fact that the process of expansion of vapor occurs so slowly that the process of formation of nuclei it is possible to consider quasi-stationary. Speed of formation moreover at each moment of time coincides with stationary speed (8.36), corresponding to actual supercooling θ, which exists in the system at a given moment.

If I(t') is the number of centers of condensation appearing in 1 sec. at moment t' (from calculation on one molecule of vapor), and g(tt') is the number of molecules at moment t in a drop of liquid which grew from the nuclei appearing at time t', then the degree of condensation by moment t x(t) it is possible to record in the form

$$x(t) = \int_{t_1}^{t} I(t')\,g(tt')\,dt'. \qquad (8.37)$$

Integration with respect to time here is conducted from the moment of saturation, i.e., from the moment when nuclei started to appear.

The speed of growth of a drop of supercritical dimensions is equal to the difference in the speeds of adhesion of vapor molecules to the surface of a drop and the evaporation of the drop. It can be approximately recorded in the form (see [19, 21])

$$\frac{dg}{dt} = 4\pi r^2 n\bar{v}\left(1 - e^{-\frac{q\theta}{T}}\right), \tag{8.38}$$

where $4\pi r^2$ is magnitude of surface of drop; $n\bar{v}$ is flux of molecules of vapor. The factor in parentheses is proportional to the difference of speeds of adhesion and evaporation. In the state of saturation, when $\theta = 0$, adhesion and evaporation compensate one another and speed of growth is equal to zero.* In supersaturated vapor $\theta > 0$ and a drop on the average grows, $dg/dt > 0$; in unsaturated vapor — $\theta < 0$ and a drop on the average evaporates, $dg/dt < 0$.

Equations (8.37), (8.38), (8.36), together with equation of adiabat of a two-phase system (8.34), by the formula of saturated vapor (8.33) and law of expansion of matter, which in the case of scattering into a vacuum is given by expression (8.25), form a full system of equations for calculating the kinetics of condensation.

In accordance with the qualitative picture presented in preceding paragraphs, the solution of this system it is possible to divide into two independent stages. The first stage is the consideration of the small interval of time immediately after achievement of a state of saturation, when supercooling at first grows, and then, passing through maximum, drops due to starting condensation. In this short stage muclei appear. Calculation of their quantity, equal to

$$\nu = \int_{t_1}^{\infty} I(t')\,dt',$$

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*Here will be disregarded the influence of curvature of drop.

gives the full number of particles of condensate (from calculation on one initial molecule). Actually integration with respect to time here spreads not to $t = \infty$, but to a very short interval of time, since in virtue of formula (8.36) speed I very sharply drops, just as supercooling, passing through maximum, starts to decrease.

The second stage is the consideration of the growth of the already known number of drops during all the subsequent stage, up to $t \to \infty$.

A strict solution of the system of equations presents, of course, great difficulties. In work [19] is an approximate solution. The approximate consideration of the first stage is based on the extraordinarily sharp dependence of $I(\theta)$, in virtue of which it is possible to consider that practically all nuclei are formed during a very short time near the moment when supercooling is maximum (solution indeed leads to an extreme form of dependence of $\theta(t)$).

Referring, for details of the solution, to work [19], we will give results of calculation for a concrete example.

Let us consider a sphere of atoms of iron with a mass of 33,000 m, which was heated and turned into dense gas, let us say, during the impact of a huge iron meteorite against the surface of the Moon. Let us assume that speed of impact was such that initial heating of iron at normal density composed $\varepsilon_0 = 72$ ev/atom. Initial temperature was $T_0 = 10$ ev $= 116,000^\circ$ K. In the stage of strong cooling by the moment of saturation vapor scatters practically inertially, with average speed $u = 15.5$ km/sec. Vapor becomes saturated at time $t_1 = 6.8 \cdot 10^{-2}$ sec from the beginning of scattering during expansion to a radius of 1050 m. With this $T_1 = 2130^\circ$ K, $n_1 = 7.15 \cdot 10^{16}$ cm^3.

In § 8 it was shown that during the scattering of initially high-ionized gas into a vacuum, there remains in it, even in the stage of strong cooling, residual ionization, which is much higher than thermodynamic equilibrium. In our example the residual degree of ionization is equal to approximately $2.1 \cdot 10^{-4}$ (equilibrium ionization by the moment of saturation would be equal to $4 \cdot 10^{-8}$). It is possible to trust that centers of condensation under conditions of such considerable ionization will contain ions. As calculations show, the number of centers of condensation very weakly depends on whether they are charged or not, so that the assumption about the fact that condensation proceeds on ions is not essential.

Maximum accessible supercooling in our example turns out to be equal to $\theta_{max} = 0.0765$ ($b/\theta_{max} = 43.1$). A nucleus of critical dimensions, with such supercooling, contains 46 atoms. The number of centers of condensation $\nu = 4 \cdot 10^{-11}$ per atom, i.e., much less than the number of ions per atom ($2.1 \cdot 10^{-4}$), in distinction from the process in a cloud chamber, where all ions become centers of condensation. Only an insignificant fraction of nuclei of the order of 10^{-5} is not charged.

Consideration of the second stage, growth of drops, shows that during a prolonged time condensation "follows" expansion of matter, and in the system there is supported a state close to saturation. Only by moment $t_2 \sim 2.5$ sec during the scattering of a sphere to 40 km, does density of matter become so small that further growth of drops ceases and hardening sets in. By this moment, and this means, only then, is condensed approximately half of iron vapor. By knowing the degree of condensation x_∞ and the number of particles of condensate, can be found also their dimensions (number of atoms in a particle is equal to $x_\infty \nu^{-1}$). In our example, to infinity scatter iron particles $3.1 \cdot 10^{-5}$ cm in radius; all of them $\sim 3 \cdot 10^{21}$.

Approximately half of the matter departs to infinity in the form of gas.

Theory permits establishing approximate laws of similarity for transition to other initial conditions. It turns out that during conditions of sufficient slowness of expansion, when initial assumptions are accurate, the degree of condensation of a given substance during scattering to infinity does not depend on initial conditions, but dimensions of particles of condensate are proportional to initial linear dimensions of an evaporated body (to the cube root of mass) and fast decrease with growth of initial heating.

§ 13. Concerning the Question of the Mechanism of Formation of Space Dust. Remarks About Laboratory Investigation of Condensation

It is necessary to realize that, considered in the preceding paragraph, the process of condensation of an evaporated substance during scattering into vacuum is one of the mechanisms of formation of space dust in the solar system (this assumption was expressed in work [19]). In interplanetary space there are little particles of various dimensions, which we call space dust. Sometimes these particles fall on Earth in the form of meteoric rain. During their revolution around the Sun, particles experience a certain braking under the effect of aberrational component of light pressure.* The

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*Light pressure itself basically acts in a radial direction. The force of pressure is inversely proportional to the square of the distance of a particle to the Sun, and its action is equivalent to only a small decrease of gravity force, i.e., the radial component of light pressure influences only the radius of orbit. Braking is caused only by a (tangent to orbit) component of light pressure, appearing due to aberration of light. For greater detail about this, see book of V. G. Fesenkov [23].

smallest particles with dimensions of the order of 10^{-6} - 10^{-5} cm fall on the Sun and disappear (see about this in [23]). Consequently, in the solar system there must exist a source making up reserves of minute particles of space dust.

It was noted (in particular, by K. P. Stanyukovich) that such a source can be the mechanical breaking up of matter during collisions of small bodies of the solar system — asteroids — or during impacts of meteorites against the surface of a planet deprived of atmosphere when particles, obtaining considerable speed, burst from the field of attraction and, not being braked in the atmosphere, depart into space.

It is possible to think that the above-described phenomenon of condensation of evaporated matter of the ground of planets, meteorites, or asteroids also is a supplier of minute particles.

During energetic collisions of asteroids, when kinetic energy of the impact is sufficient for the full evaporation of both colliding bodies, the mechanical effect of the breaking up of solid matter, in general, is absent since all mass is completely evaporated. In this case, for the formation of minute particles there is only the mechanism of condensation.

Liquid drops, growing during condensation, gradually cool thanks to losses of energy on thermal radiation and harden. It is possible to show that the process of cooling by radiation proceeds much faster than evaporation of heated particles, which is very sharply delayed according to cooling. Thus, once born, particles of condensate will continue their existence in the form of hard dust motes. Inasmuch as in the cosmos there occur collisions of bodies of the most varied dimensions and speeds, there are born particles of condensate also of the most varied dimensions.

The phenomenon of condensation of evaporated matter during gas-dynamic expansion it is possible to use also for laboratory study of condensation of the vapor of metals or other solid (and liquid) substances and the study of optical properties of minute particles.

Dimensions of particles of condensate depend on initial conditions; therefore, by means of corresponding selection of these conditions it is possible to obtain, in the laboratory, particles of desirable dimensions. Let us give results of a rough estimate for conditions close to laboratory conditions. If one were to quickly evaporate 1 g iron, having imparted to it, by any means, initial energy of $\varepsilon_0 = 13$ ev/atom corresponding to initial temperature (during density of hard metal) $T_0 = 35{,}000^\circ$ K, then condensation of vapor during scattering into a vacuum (in an evacuated vessel) is finished by moment $t = 5 \cdot 10^{-5}$ sec during the scattering of a small cloud 30 cm. Particles of condensate have dimensions of the order of 10^{-4} cm.

Calculations of kinetics of condensation are easily transposed also to other possible laws of expansion of matter, which take place, let us say, in a wind tunnel or during expiration from a jet. These calculations do not contain anything new in principle, as compared to the case of scattering into a vacuum, and we will not pause on them. Let us note that if degree of condensation of vapor is small or total energy of vapor is much larger than heat of evaporation, condensation shows little on gas dynamics of the process. Kinetics of condensation it is possible to calculate on the basis of the known gas-dynamic solution found in the first approximation, without taking into account condensation. Just as we did in the preceding paragraph.

Literature

1. A. Kantrowitz. J. Chem. Phys., 10, 145 (1942); 14, 150 (1946).

2. M. H. Bloom and M. H. Steiger. J. Aero Space Sci., 27, 821 (1960). Translation: Problem of Rocket Technology, No. 5 (1961).

2a. Li Ting-Y. ARS J. 31, 170, 1961.

3. H. O. Kneser. Ann. der Physik, 11, 761 (1931).

4. H. O. Kneser. Ann. der Physik, 11, 777 (1931).

5. A. Einstein. Sitzungsber. Berliner Akad. der Wissensch., 1920, p. 380.

6. V. F. Nozdrev. Application of ultrasonics in molecular physics, Fizmatgiz, 1958.

7. G. S. Gorelik. Oscillations and waves, Fizmatgiz, 1959.

8. L. I. Mandel'shtam and M. A. Leontovich. ZhETF, 7, 3, 1937.

9. L. I. Landau and Ye. M. Lifshits. Mechanics of solid matter, State Technical Press, 1954.

10. L. Landau and E. Teller. Phys. Z. Sowjetunion, 10, 34 (1936).

11. V. L. Ginzburg. Acoustical Journal, 1, 31 (1955).

12. The Effects of Atomic Weapons, New York — Toronto — London, 1950.

13. Yu. P. Rayzer. Journal of Physical Chemistry, 33, 700 (1959).

14. Ya. B. Zel'dovich, P. Ya. Sadovnikov, and D. A. Frank-Kamenetskiy. Oxidation of nitrogen during burning, Publishing House of Academy of Sciences of USSR, 1947.

15. V. A. Tsukerman and M. A. Manakova. ZhETF, 27, 391 (1957).

15a. P. Molmud. Phys. Fluids, 3, 362 (1960).

16. V. A. Belokon'. Proceedings of MFTI, No. 11 (1963).

17. Yu. P. Rayzer. ZhETF, 37, 580 (1959).

18. L. Landau and Ye. Lifshits. Statistical physics, State Technical Press, 1951.

19. Yu. P. Rayzer. ZhETF, 37, 1741 (1959).

20. Ya. B. Zel'dovich and Yu. P. Rayzer. ZhETF, 35, 1402 (1958).

21. Ya. I. Frenkel'. Kinetic theory of fluids, Publishing House

of Academy of Sciences of USSR, 1945.

22. Ya. B. Zel'dovich. ZhETF, 12, 525 (1942).

23. V. G. Fesenkov. Meteoric matter in interplanetary space, Publishing House of Academy of Sciences of USSR, 1947.

24. R. Narasimha. J. Fluid Mech., 12, 294 (1962). Translation: Mechanics, No. 2 (1963).

25. A. Ya. Pressman. DAN USSR, 138, 1305 (1961).

CHAPTER IX

LIGHT PHENOMENA IN SHOCK WAVES AND DURING STRONG EXPLOSION IN AIR

1. Brightness of Front of Shock Waves of Great Amplitude in Gases

§ 1. Qualitative Dependence of Luminance Temperature on True Temperature after the Front

Optical measurements have great value for determination of temperature of highly heated bodies and, in general, for investigation of high-temperature processes. The usual method consists of measuring, in some manner, the brightness of the surface of a luminescent body (by photographic means, with the help of photocells, electron-optical multipliers). Then by the brightness find the effective temperature of radiation, which, by definition, coincides with the temperature of an ideal black radiator sending from the surface precisely the same luminous flux as the investigated object (see § 8, Chapter II). Especially wide-spread are photographic methods of determining brightness and effective temperature, founded on a comparison of degrees of blackening, which produce on photographic film light emanating from the body and light from a standard source with known temperature and spectrum, let us say, from the sun. For greater accuracy we photograph usually in a narrow spectrum section, since the studied object and the standard source, possessing different temperatures, send different spectra of radiation, and furthermore, on the wave length of the light depends sensitivity of photographic material, which creates difficulty during recalculation of degree of blackening by temperature.

Optical (in particular, photographic) methods are widely applied also during the study of shock waves. Gas, heated in a strong shock wave to high temperature, radiates, and the surface of the front of the wave gleams. The brightness of the glow depends on the amplitude of the shock wave and the dimensions of the heated region after the front. So that effective or actual luminance temperature, measured during the experiment, can be judged relative to true temperature of substance after the front of the wave, confidence is necessary in the fact that a luminescent object radiates as an ideal black body.

If the front of the shock wave constitutes a "classical" jump and after it spreads a quite extended, optically thick region with more or less constant temperature equal to the temperature after the front, then heated matter, limited by the surface of the front, radiates from the surface as an ideal black body.* Measuring the brightness of the surface of the front, it is possible in such a case to

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*If the region of heated gas after the "classical" jump is optically thin (for instance, the shock wave departs only a small distance from the piston creating it, inserted in the gas), the gas emits light as a volume radiator. Luminous flux, outgoing from the surface of the optically thin layer in the direction of normal to the surface, is equal, as was shown in § 7, Chapter II, to: $S_\nu = S_{\nu p} [1 - \exp(-\varkappa'_\nu d)]$, where $S_{\nu p}$ is flux corresponding to an ideal black body of the same temperature, $\varkappa'_\nu$ is the coefficient of absorption, and d is the thickness of layer heated by shock wave. During small optical thickness $\varkappa'_\nu d \ll 1$, $S_\nu = S_{\nu p}\varkappa'_\nu d \ll S_{\nu p}$. In a limit of $\varkappa'_\nu d \gg 1$ flux aspires to Planckian $S_\nu = S_{\nu p}$. As was noted in § 21, Chapter V, while studying the build-up of brightness S_ν in time $t = d/D$ (D is speed of wave), I. Sh. Model' measured the coefficients of absorption of red light in a shock wave [1].

determine directly the temperatures after the front of a shock wave, i.e., amplitude of wave, which is important not only for experimental investigations but, also, it has great practical value. Experience shows that in a certain range of amplitudes (and, of course, during sufficiently great thickness of heated region after the front) the front of a shock wave, indeed, radiates as a black body. This is confirmed by the fact that luminance temperature coincides with temperature after the front, calcúlated on the basis of shock relationships and equation of state along one of the other experimentally determined parameters of the front, let us say, by speed of propagation of the shock wave.

However, experiments and theoretical consideration show that such coincidence cannot be observed at any amplitudes. Luminance temperature of a sufficiently strong shock wave becomes less than true temperature after the front, where starting from a certain amplitude, it drops very fast during growth of amplitude; it attains a limiting, comparatively low value and, subsequently, hardly changes during any amount of large increase of amplitude. Typical dependence of luminance temperature of the front of a shock wave on true temperature after the front is depicted in Fig. 9.1, where is represented a curve, obtained on the basis of theoretical appraisals (made in the following paragraphs), of effective temperature of red light for a shock wave in air of normal density. Fig. 9.1 testifies to the existence of the effect of "saturation" of brightness. However strongly gas is heated by a shock wave, even up to a million degrees, nevertheless it is impossible to "see" a temperature higher than hundreds of thousands of degrees; there exists an upper limit of temperature after the front of a shock wave, which it is possible to "see".

This effect can be easily explained on the basis of concepts about the structure of the front of a shock wave, taking into account the radiation presented in § 3, Chapter VII. The question on brightness of front of shock waves of great amplitude was considered in the works of authors [2-4].

We will consider that after the front of a flat shock wave there spreads a sufficiently extended, optically thick region with a constant high temperature, and we will observe what kind of flux of visible radiation, which emerges from the surface of the front of the wave and is recorded by an instrument, is located far from the front, at "infinity".

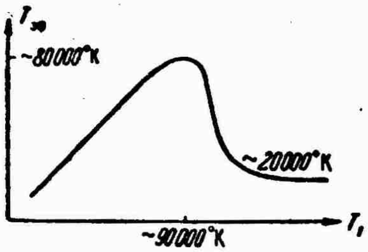

Fig. 9.1. Dependence of luminance temperature of the surface of the front of a shock wave in the air on true temperature after the front (for red light).

Let us consider at first a shock wave not too great in amplitude, in which the role of radiation is insignificant and there is no heating of gas before compression shock. If one were to digress from the change of temperature in the front, connected with relaxation processes in gas, then the distribution of temperature in the shock wave constitutes the "classical" jump, shown in Fig. 9.2a. Thickness of jump, together with relaxation layer, usually is much less than range of radiation; therefore, we have a typical example of an ideal black radiator: an optically thick layer of heated (to constant temperature T_1) matter is limited by a surface with a very sharp jump of temperature. If cold gas is before the front, as usually occurs, it is transparent in the visible part of the spectrum (is colorless); the instrument will register luminous flux, corresponding to Planckian radiation of temperature T_1; the effective temperature of radiation will be equal to the true temperature of gas after the front.

Let us consider now a shock wave of great amplitude, let us say, with temperature after the front of $T_1 = 65{,}000^\circ K$. From the surface of shock discontinuity, basically, there are radiated quanta with energies of the order of ten or several tens of ev. (Maximum of Planckian spectrum at a temperature of $T = 65{,}000^\circ K$ was apportioned to quanta $h\nu = 2.8\ kT = 16$ ev). Such quanta exceed ionization potentials of atoms and molecules, are very strongly absorbed in cold gas before shock discontinuity, and heat it. Before the shock discontinuity there will be formed a heated layer, and the profile of temperature in the shock wave obtains the form depicted in Fig. 9.2b (in air, for instance, during $T_1 = 65{,}000^\circ K$ maximum temperature of heating before the actual shock is $T = 9000^\circ K$).

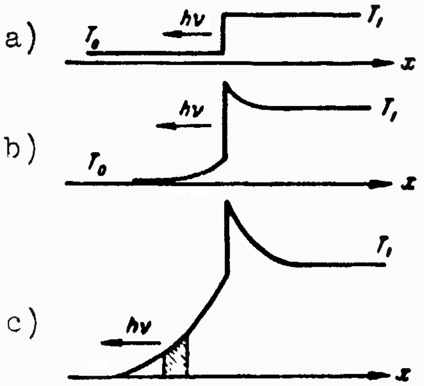

Fig. 9.2. Concerning the question of glow of a shock wave.

In distinction from cold, heated gas always absorbs little quanta of visible light ($h\nu \sim 2$-3 ev). In monatomic gases, quanta smaller than ionization potential of atoms I, are absorbed by excited atoms, whose excitation energy exceeds $I - h\nu$; in accordance with the law of Boltzmann, concentration of excited atoms is proportional to $\exp\left[-\frac{I - h\nu}{kT}\right]$, so that coefficient of absorption very sharply, by Boltzmann law, increases with increase of temperature $\varkappa_\nu \sim \exp\left(-\frac{I - h\nu}{kT}\right)$. In molecular gases, such as air, there is still a number of other mechanisms of absorption of visible light; in any case the coefficient of absorption of visible light is always very sensitive to temperature and grows fast during heating.

Now the quanta of visible light, which are radiated from the surface of the shock discontinuity and whose flux for the actual shock corresponds, roughly speaking, to temperature T_1,* before getting on the recording instrument located at "infinity", have to penetrate through heated layer. They are partially absorbed in this layer. Therefore, the effective temperature of visible radiation of the front of the shock wave will be less than true temperature after the front: the heated layer, as it were, shields the highly heated gas after the front of the shock wave. Shielding and, consequently, deflection of T_{ef} from T_1 is stronger, the greater the optical thickness of the heated layer for visible light τ_ν,** i.e., the higher the temperature of heating and the higher the amplitude of the wave.

While optical thickness $\tau_\nu << 1$, shielding is insignificant, and deflection of T_{ef} from T_1 is very small; the front gleams as a black body of temperature T_1. Because of the clear dependence of absorption of visible light on temperature and, in turn, the rather sharp dependence of temperature of heating on amplitude of wave (see § 16, Chapter VII), the beginning of strong shielding, corresponding to the achievement of optical thickness τ_ν of a magnitude of the order of unity, very clearly sets in during growth in amplitude of wave. In air strong

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*In reality the flux of quanta is somewhat larger, since directly after the discontinuity the temperature is higher than the temperature after the front (see Fig. 9.2b).

**It is emphasized that optical thickness of the heated layer for visible radiation τ_ν has nothing in common with (averaged over the spectrum) optical thickness of the layer corresponding to the large quanta "controlling" the heating. As was shown in § 16, Chapter VII, temperature in the heated layer drops approximately exponentially with respect to averaged optical thickness $T = T_- \exp(-\sqrt{3}|\tau|)$ (at $T_- < T_1$), so that averaged thickness of the layer is of the order of unity.

shielding starts at a temperature after the front of near $T_1 = 90,000^\circ K$ (see § 3).

In a shock wave of still larger amplitude, optical thickness of heated layer for visible light is larger than unity, and the layer is almost absolutely opaque for visible quanta radiated by highly heated gas after the front of the wave: shielding of this region is almost full. Thus, with increase of amplitude of wave, effective temperature of visible light in the beginning coincides with temperature after the front, then starts to lag behind it, passes through a clearly expressed maximum ("saturation" of brightness) and fast drops.

The appearance of strong shielding by the heated shell does not signify, however, that the brightness of the front of a shock wave of very great amplitude drops to zero and the wave ceases to gleam. Heated gas before a shock discontinuity not only absorbs but radiates visible light itself. While the temperature of heating is not very high and the shell is transparent, intrinsic emission of it is lost against the background of passing visible radiation, emitted by the much more strongly heated gas after the front. When the heated layer absolutely ceases to pass the high-temperature light, to the first plane comes forward its intrinsic radiation.

In order to obtain an idea on the brightness of this intrinsic radiation of the heated layer, let us note that the temperature in it monotonically increases, starting from "zero," more exactly, from the temperature of the cold gas before the front. Due to sharp temperature dependence of absorption of visible light in the most forward layers of the zone of heating, where the temperature is low, light is not absorbed and is not radiated. In deeper layers during high temperature visible quanta are intensely emitted, but right here again they are absorbed, being not in a state to emerge outside in virtue of opacity of gas. To "infinity" from the surface of the front there emerge quanta, generated in a certain intermediate, radiating shell of the heating zone, distant from "infinity" at an optical distance (corresponding to frequencies of visible light) of the order of unity. In Fig. 9.2c radiating layer is shaded. Obviously, effective temperature of radiation coincides with average temperature of radiating layer. The position of the layer is determined only by the profile of the temperature of gas T (x) and by temperature dependence of absorption $\varkappa_\nu$ (T) on the condition that the layer will stand from the cold gas at an optical distance of the order of unity. As was shown in § 17, Chapter VII, profile of temperature on the front edge of the heated zone in shock waves of great amplitude hardly depends on amplitude of wave. Consequently, also not dependent on amplitude is intrinsic radiation of the heated layer, i.e., effective temperatures of a very strong shock wave. In air of normal density this limiting luminance temperature in red light is equal approximately to 20,000°K (see § 4).

The effect of shielding and the sharp understating of luminance temperature of the front of the shock wave, as compared to true temperature after the front, was observed experimentally by I. Sh. Model' [1]. In his experiments, by photographic means was measured luminance temperature of the front of shock waves in heavy inert gases — xenon, krypton, and argon — in which it is possible to obtain high temperatures in a shock wave. Speed of the front in these experiments was equal to 17 km/sec. Optical thickness of the heated region after the front of the shock wave was known to be great, so that in the absence of shielding the front had to radiate as a black body. However, by experiment was observed a luminance temperature of 30,000-35,000°K, which was several times lower than the temperatures after the front T_1, calculated by speed of front and shock relationships (in Xe — $T_1 \approx$ $\approx 110{,}000^{\circ}K$, in Kr — $T_1 \approx 90{,}000^{\circ}K$, in Ar — $T_1 \approx 60{,}000^{\circ}K$). If one were to consider that the accuracy of experimental determination of effective temperature of visible (red) light was not less than ±20%, then the shown divergence must be attributed, namely, to the shielding by the heated layer. Unfortunately, in experiments of I. Sh. Model' there was recorded only one point with respect to amplitude of wave that does not give the possibility of tracing the character of the entire curve of dependence of luminance temperature on true temperature after the front.

It is necessary to note that the phenomenon of "saturation" of brightness during high temperatures was observed by many authors in spark discharge.* It is known that increase of entering speed of energy into channel of spark discharge, starting from a certain speed, does not lead to increase of luminance temperature higher than $\sim 45{,}000^{\circ}K$ in air. Also limited is the temperature of glow and during discharge in argon, xenon (during discharge in capillaries higher temperature is observed — near $90{,}000^{\circ}K$ in air).

At present it is still impossible with confidence to judge the nature of this effect of saturation: whether it is connected with shielding of high temperatures in the channel, in what measure is there similar shielding in a shock wave, and whether true temperature is limited in the channel at the expense of losses on radiation, etc.

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*Source material can be found in the survey of M. P. Vanyukov and A. A. Mak [5] about strobe lights of high brightness, and also in the work I. Sh. Model' [1].

§ 2. Absorption of Light Quanta in Cold Air

Of especially great practical interest is the question on brightness of strong shock waves in air of normal density, which we will consider more specifically. It is necessary to determine the upper boundary of amplitude interval in which the front of a shock wave radiates visible light as an ideal black body and to estimate maximum and limiting luminance temperature. The problem leads, obviously, to an appraisal of the optical thickness of heated layer for visible radiation, which determines degree of shielding of highly heated region after the front, and to finding the intrinsic radiation of the heated layer.

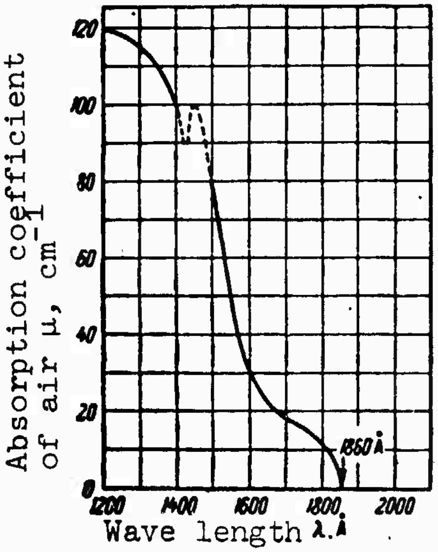

Fig. 9.3. Coefficient of absorption of ultraviolet radiation in cold air.

For this it is necessary, first of all, to definitize the geometric thickness of the heated layer and the distribution of temperature in it with respect to geometrical coordinate, which, in turn, depends on how there are absorbed in the air comparatively large quanta with energies of the order of tens to hundreds of ev, responsible for heating of gas before the shock discontinuity. Let us summarize data known from literature about the absorption of such quanta in cold air.

Above we have repeatedly noted the well-known fact that cold air is absolutely transparent for visible light. Noticeable absorption starts in the ultraviolet region of the spectrum at wave length

$\lambda = 1860\ \mathring{A}$ ($h\nu = 6.7$ ev).* For absorption is responsible a system of Schuman-Runge bands of oxygen molecule, which at $\lambda = 1760\ \mathring{A}$ ($h\nu = 7.05$ ev) passes into continuum, connected with dissociation of molecule during absorption of light. Absorption fast increases with increase of energy of quanta (at $\lambda = 1860\ \mathring{A}$ $\varkappa_\nu = 0.0044\ cm^{-1}$), and at $h\nu \approx 8$ ev attains a magnitude of the order of $\varkappa_\nu \approx 100\ cm^{-1}$. The experimental curve of the dependence of the coefficient of absorption on wave length in this region of the spectrum is shown in Fig. 9.3.** Quanta exceeding ionization potentials of molecules of oxygen and nitrogen $I_{O2} = 12.1$ ev, $I_{N_2} = 15.6$ ev, experience strong photoelectric absorption. Effective absorption cross sections from basic level of molecules weakly depend on frequency in the range of energies from $h\nu = I$ and $h\nu \sim 25$ ev and are equal approximately to $\sigma_O = 3.10^{-18}\ cm^2$, $\sigma_N = 5.10^{-18}\ cm^2$, which gives coefficient of absorption $\varkappa_\nu \approx 120\ cm^{-1}$. During further increase of frequency, coefficient of absorption should experience jumps connected with successive inclusion in the absorption of different electrons filling L-shell of atoms of nitrogen and oxygen. Levels in the L-shell, apparently, will be not too far from each other, so that jumps, probably, lie in the region of energies $h\nu$ from 13 to 30-40 ev (experimental data about jumps, as far as we know, are lacking).

After that, the coefficient of absorption monotonically drops with increase of frequency up to energy of quanta $h\nu_k = 410$ ev, equal K-binding energy of nitrogen atom (for oxygen boundary of K-absorption

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*Strong absorption of close ultraviolet solar radiation in the region $\lambda \sim 2000\text{-}3000\ \mathring{A}$ is connected with the existence of an ozone layer at a height of ~ 25 km. Oxygen and nitrogen do not absorb in this part of the spectrum; therefore, talking about shock waves in air near the surface of Earth, one should establish upper boundary of transparency of air for $\lambda \sim 1860\ \mathring{A}$.

**The curve is taken from the work Schneider [6].

$h\nu_k^{\prime} = 530$ ev). During energy $h\nu_k = 410$ ev absorption coefficient sharply increases, since quanta larger than $h\nu_k$ are able to knock out K-electrons from atoms of nitrogen, but then monotonically drops to $h\nu_k^{\prime} = 530$ ev, when in absorption are included K-electrons of oxygen. Coefficients of absorption of quanta $h\nu_k = 410$ ev before and after jump of K-absorption in nitrogen, calculated according to [7, 8], are equal to 1.6 cm^{-1} and 35 cm^{-1}. Experimental material on absorption of air in the intermediate region of frequencies from tens to hundreds of ev is extraordinarily scanty: measurements, as far as we know, were done only for two lines, $h\nu = 182$ ev [9] and $h\nu = 280$ ev [10].

On the basis of all this fragmentary information is composed a table which gives a more or less graphic presentation about coefficients of absorption and mean free paths of quanta in tens and hundreds of ev in cold air of normal density.

Table 9.1

$h\nu$, ev	8	13—25	182	280	410 Before Jump	410 After Jump
$\varkappa_\nu$, $см^{-1}$	100	~120	12	5,3	1,6	35
l_ν, см	0,01	0,0083	0,083	0,19	0,63	0,029

§ 3. Maximum Luminance Temperature for Air

In § 16, Chapter VII it was shown that if amplitude of the shock wave is less than critical (and in air of normal density, critical amplitude corresponds to temperature after front of $T_1 \approx 285{,}000°K$), then the transfer of radiation from the highly heated region after the front to layers located before the shock discontinuity does not have diffusion character. The air in them is heated to temperatures much lower than the temperature after the front, and emission of radiation in the zone of heating introduces practically no contribution to the passing radiation flux, generated after the discontinuity. Air is heated simple in virtue of the absorption of passing quanta at distances of the order of mean free paths for absorption, and thickness of zone of heating Δx in order of magnitude is equal to the mean free path of l those quanta which carry the basic energy of the spectrum. Mathematically this is expressed by formula (7.55), determining exponential drop of heating with respect to averaged optical thickness τ, corresponding to a certain coefficient of absorption $\varkappa = 1/l$, averaged over the spectrum:

$$\varepsilon = \varepsilon_{-} e^{-\sqrt{3}|\tau|}, \quad \tau = \int_0^x \varkappa\, dx^{*} \qquad (9.1)$$

This formula shows that effective optical thickness of heated layer is of the order of unity, i.e., geometric thickness is of the order of $\Delta x \sim 1/\varkappa = l$.

From the table in the preceding paragraph it follows that mean free paths of quanta with energies of the order of 10-100 ev in cold air change from 10^{-2} to 10^{-1} cm.

It is easy to see that the mean free paths of these quanta are such approximately even in not too strongly heated air in the zone of heating.

Let us consider, for instance, a shock wave with a temperature after the front of $T_1 = 65{,}000^\circ K$. Maximum of Planckian spectrum was apportioned to quanta $h\nu = 16$ ev, i.e., a considerable part of the energy of the spectrum is concentrated in an energy band from quanta exceeding ionization potentials of atoms and molecules $h\nu > I \approx 13$ ev.

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*Formula (7.55) is recorded not for specific internal energy but for temperature. Formula (9.1) is more general; it is accurate even in those cases when heat capacity depends on temperature, as takes place in air.

The biggest temperature of heating, as Table 7.2 shows is $T_- = 9000^\circ K$. With such a temperature degree of ionization and excitation of atoms is small, i.e., quanta $h\nu >> I$ are absorbed practically the same as in cold air. If one were to take a more powerful shock wave, let us say, with a temperature after the front of $T_1 = 100,000^\circ K$, then maximum of the spectrum corrssponds to quanta $h\nu = 24$ ev and basic energy of the spectrum is concentrated in the region of higher energies of quanta, of the order of several tens of ev.

At a temperature of heating $T_- = 25,000^\circ K$, first ionization of atoms is noticeable, but second is virtually lacking. Quanta with energies of several tens of ev knock out from atoms, mainly, not the external, optical electrons, but the more deeply lying electrons, which at a temperature of $\sim 25,000^\circ K$ still are not touched by thermal ionization and excitation. Thus, in this case, quanta carrying out heating are absorbed approximately the same as in cold air.

Hence there can be made the conclusion that the thickness of the zone of heating before a shock discontinuity in waves of subcritical amplitude ($T_1 < 285,000^\circ K$) has the order of the mean free paths of ten - one hundred electron volt quanta in cold air, i.e., $\Delta x \sim 10^{-2} - 10^{-1}$ cm. With this Δx is increased in shown limits, if one were to pass to waves of even greater amplitude in a range of temperatures after the front from tens of thousand of degrees to $T_1 \sim 200,000^\circ K$, which corresponds to a shift in the characteristic energies of quanta from $h\nu \sim 10$-30 ev to $h\nu \sim 30$-100 ev.

We will consider now how far visible light shields the heating zone. In Table 9.2 are given coefficients of absorption and mean free paths of red light $\lambda = 6500\ \mathring{A}$ in air of normal density at different temperatures.

Table 9.2

$T \cdot 10^{-3}$, °K	15	17	20	30	50	100
$\varkappa_\nu$ см$^{-1}$	4,1	13,5	60	290	350	2000
l_ν см	0,25	$7,4 \cdot 10^{-2}$	$1,66 \cdot 10^{-2}$	$3,45 \cdot 10^{-3}$	$2,85 \cdot 10^{-3}$	$5 \cdot 10^{-4}$

Noticeable shielding sets in when mean free path l_ν, fast decreasing with temperature rise, becomes comparable with the thickness of the zone of heating, i.e., with the mean free path of heating radiation l (average over the spectrum). Let us introduce for convenience the idea of "temperature of transparency" T*, which we will define as condition

$$l_\nu(T^*) = l. \qquad (9.2)$$

The meaning of this idea is obvious: temperature of transparency differentiates two temperature ranges in a shock wave. At $T < T^*$ $l_\nu > \Delta x$ and air in the zone of heating is transparent for visible light. At $T > T^*$ $l_\nu < \Delta x$ and air is opaque.

Inasmuch as absorption of visible light very sharply depends on temperature, and averaged mean free path changes comparatively little (only by one order), defined by equality (9.2), the temperature of transparency is included in quite narrow limits, namely: $T^* \approx \approx 17{,}000$-$20{,}000^\circ$K. It is possible to estimate optical thickness of the zone of heating for visible light, assigning for simplicity Boltzmann temperature dependence of the absorption coefficient of visible light $\varkappa_\nu = \text{const} \cdot \exp\left(-\frac{I - h\nu}{kT}\right)$ and considering average coefficient of absorption $\varkappa$ to be constant. Considering that internal energy of air at normal density and temperatures of the order of tens of thousands of degrees, roughly speaking, is proportional to $\varepsilon \sim T^{1.4}$, with the help of formula (9.1) we will find approximately the optical thickness in the heated zone from "infinity" (i.e., from the region of cold air) to a point with temperature T: τ_ν (T)(full optical thickness of the zone of heating is τ_ν (T_-))

$$\tau_\nu(T) = \int_{-\infty}^{x} \varkappa_\nu \, dx = \int_{0}^{T} \varkappa_\nu \frac{dx}{dT} \, dT = \int_{0}^{T} \frac{\text{const}}{\varkappa} \frac{1.4}{\sqrt{3}} e^{-\frac{I-h\nu}{kT}} \frac{dT}{T} \approx$$
$$\approx \frac{1}{\varkappa} \frac{1.4}{\sqrt{3}} \frac{kT}{I-h\nu} \cdot \text{const} \cdot e^{-\frac{I-h\nu}{kT}} = \frac{1.4}{\sqrt{3}} \frac{kT}{I-h\nu} \frac{\varkappa_\nu(T)}{\varkappa}. \qquad (9.3)$$

In a shock wave with $T_1 = 90{,}000°K$, in which temperature before discontinuity is equal to temperature of transparency $T_- = T^* = 20{,}000°K$, optical thickness of the zone of heating is equal, in accordance with determination of temperature of transparency (9.2), to $\tau_\nu = 0.81 \frac{kT^*}{I - h\nu} \approx 0.12$ ($I \approx 14$ ev, $h\nu \approx 2$ ev).

Consequently, if one were to look at the surface of the front of a shock wave in a direction normal to surface, flux of visible radiation, outgoing from the surface of shock discontinuity, will be weakened by the heated layer approximately 12%, and effective temperatures, instead of 90,000°K, will be equal to approximately 80,000°K (with such temperatures little visible quanta lie in the Rayleigh-Jeans part of the spectrum, and their intensity is proportional to first degree of temperature; therefore, effective temperature is simply proportional to brightness).

During further increase of amplitude of wave the optical thickness of the layer grows and brightness drops; for instance, with increase of temperature after the front by only 10,000°K at $T_1 = 100{,}000°K$, $T_- = 25{,}000°K$, τ_ν (T_-) ≈ 0.37, $T_{ef} \approx T_1 e^{-0.37} \approx 67{,}000°K$, i.e., effective temperature is already less than 80,000°.

Maximum of brightness corresponds to temperature after the front near $T_1 = 90{,}000^{\circ}K$, and maximum effective temperature is equal approximately to $T_{ef\ max} = 80{,}000^{\circ}K$.* At a temperature after the front of $T_1 = 140{,}000^{\circ}K$, $T_- \approx 50{,}000^{\circ}K$, $\tau_{\nu}(T_-) \approx 1.5$, and shielding is almost complete.

§ 4. Limiting Brightness of a Very Strong Wave in Air

We will estimate the intrinsic radiation of the heated layer in a wave of great amplitude, determining the limiting brightness of the front of the shock wave. Let us consider a shock wave of supercritical amplitude with a temperature after the front much higher than critical, equal to $285{,}000^{\circ}K$. In § 17, Chapter VII it was shown that distribution of temperature in the front of a wave with respect to averaged optical thickness τ has the form depicted in Fig. 9.4. The temperature of heating before the actual shock discontinuity coincides with the temperature after the front T_1. Temperature in the heated layer monotonically drops to temperature of cold air, where averaged optical thickness of all the zone of heating can be very great; it is even greater the higher the amplitude of the wave. The main part of the zone of heating is composed of a region with temperatures from $T_- = T_1$ and up to temperature of the order of critical $T_k \approx 300{,}000^{\circ}K$. This part of the zone, inherently, will be expanded with increase of amplitude (see Fig. 9.4).

On the front edge of the zone, where the temperature is lower than $300{,}000^{\circ}K$, distribution of temperature, just as in the

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*We emphasize that all these values are estimates since coefficients of absorption of visible light in heated air, calculated by the formula Cramer, cannot be recognized as fully reliable.

subcritical zone, has an exponential character and hardly depends on amplitude:

$$\varepsilon = \varepsilon_k e^{-\sqrt{3}|\tau-\tau_k|}, \quad T = T_k e^{-\frac{\sqrt{3}}{1.4}|\tau-\tau_k|} \tag{9.4}$$

(see § 17, Chapter VII, formula (7.64), and also Fig. 9.4; optical coordinate τ_k pertains to a point where temperature is equal approximately to $T \approx T_k \approx 300,000^{\circ}$K).

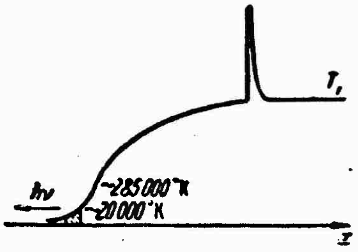

Fig. 9.4. Position of a radiating layer (shaded) in a shock wave of very great amplitude.

At the end of § 1 it was noted how a body with similar distribution of temperature radiates visible light. At low temperatures the air is transparent and does not radiate; at high — it is absolutely opaque and does not "release" outside visible quanta. The radiating layer, which sends basically flux of visible light to "infinity," in cold air, lies somewhere between transparent and opaque regions (it is shaded in Fig. 9.4). The temperature in the radiating layer, obviously, is close to the temperature of transparency of air, defined by equality (9.2), where l is the mean free path, average over the spectrum, in the region where lies the radiating layer. Luminance temperature of visible radiation also approximately coincides with temperature of transparency. If the average mean free path, as before, is included in the interval $10^{-2} - 10^{-1}$ cm, then limiting luminance temperature should be equal to 17,000-20,000°K (see Table 9.2).

Let us be convinced of the fact that this appraisal is indeed accurate, in other words, of the fact that heating on the front edge of the zone of heating in a very strong shock wave is carried out by quanta which have namely such a mean free path. For this, let us note that at temperatures higher than critical in the zone of heating local equilibrium takes place, but at lower temperatures radiation is nonequilibrium just as in the heated layer of a subcritical shock wave.

Approximately, one may assume that from a surface where temperature is equal to $T_k \approx 300,000^\circ K$, to the left (see Fig. 9.4) goes out Planckian spectrum of radiation of such a temperature, independently of how high temperature rises after this surface.

The general tendency of absorption of large quanta corresponding to a spectrum with temperature of $300,000^\circ K$ (maximum of spectrum was apportioned to quanta $h\nu \approx 70$ ev), is such that coefficient of absorption $\varkappa_\nu$ drops with growth of frequency. As can be seen from Table 9.1, in energy band of quanta in hundreds, electron volt $\varkappa_\nu$ monotonically decreases with increase of frequency. Therefore, when moving in the direction of a temperature decrease from a surface where $T = 300,000^\circ K$, in the beginning small quanta are absorbed, then more energetic quanta. As it moves toward a region of low temperatures the spectrum becomes harder and harder. Calculation made in work [4] shows that into the region of temperatures of the order of transparency temperatures, where, as we expect, lies radiating layer, penetrate only very hard quanta with energies $h\nu \approx 200$ ev. In Table 9.3 are presented energies of quanta "conducting" heating in the region of low temperatures on the front edge of the zone of heating. In the same place are shown also mean free paths corresponding to these quanta, exactly equal to mean free paths approximately averaged over the spectrum.

We see that in the region of temperatures $T \sim 20,000^\circ K$ the average mean free path is $l \sim 10^{-1}$ cm, i.e., temperature of transparency is faster closer to $17,000^\circ K$.

Table 9.3

T° K	h_ν, ev	l, см	$\varkappa$, см$^{-1}$
50 000	140		
20 000	200	$0{,}95\cdot10^{-1}$	10,5
15 000	212	$1{,}02\cdot10^{-1}$	9,8
10 000	225	$1{,}16\cdot10^{-1}$	8,6

Thus, the limiting luminance temperature of a very strong shock wave is equal approximately to 17,000°K, independent of amplitude. The general dependency of luminance temperature (in red light) on temperature after the front is shown in Fig. 9.1. It is necessary to note that coefficients of absorption in the visible region of the spectrum rather weakly depend on frequency; therefore, estimated values of luminance temperatures approximately pertain not only to red, but, in general, to all the visible region of the spectrum.

2. Optical Phenomena, Observed During Strong Explosion, and Cooling of Air by Radiation

§ 5. General Description of Light Phenomena

During an atomic explosion in air there are obtained a powerful shock wave and very high temperatures. Temperature after the front of the wave passes through a continuous series of values in a wide range from hundreds of thousand of degrees to normal. During explosion there is observed a series of interesting and very unique optical phenomena. Below is presented the general description of the physical process of development of an explosion in air, near the surface of the earth (i.e., in air of normal density). This description is completely borrowed from the American book "The Effects of Atomic Weapons" [11], issued in 1950.*

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*We quote points 2.1; 2.6-2.22; 6.2; 6.19; 6.20 of the second and sixth chapters of the book and also present photograph 2 and Figs. 6.6; 6.18; 6.20. In 1957 in the United States there appeared a second publication of this book, which was translated into the Russian language [12]. The second publication was revised, as compared to the first. In it are considerably expanded divisions concerning the destructive action of the explosion, but divisions dedicated to the description of

During nuclear fission of uranium or plutonium, in an atomic bomb there occurs emanation of huge energy content in minute initial volume during a very short interval of time. Subsequently we will consider that energy liberated during explosion of the bomb is approximately equivalent to energy liberated during an explosion of 20,000 tons of trotyl, which is nearly 10^{21} erg (more exactly, $8.4 \cdot 10^{20}$ erg). Such a bomb is called a nominal atomic bomb. As a result of the extraordinarily high concentration of energy, the temperature of fissionable material attains a million degrees. Inasmuch as the explosion occurs in the limited volume occupied by the bomb, pressure sharply increases and attains several hundreds of thousands of atmospheres.

When heating up a substance to extraordinarily high temperature, there occurs energy release in the form of electromagnetic radiation, whose spectrum embraces a wide range of wave lengths spreading from infrared (thermal) rays through the visible region of the spectrum to the region of ultraviolet rays and emerges beyond its limits. A large part of the radiation is absorbed in layers of air directly adjoining the bomb, as a result of which air is heated to a glow. Thus, several microseconds after the explosion the exploding bomb obtains the form of a luminescent sphere, called a fiery sphere.

According to propagation radiant energy heats ambient air; as a result the fiery sphere is increased in dimension, but temperature, pressure, and brightness correspondingly decrease. Upon expiration of

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[FOOTNOTE CONT'D FROM PRECEDING PAGE].
the physical phenomena in the fiery sphere are shortened. Inasmuch as we here are interested in namely these last questions, we will borrow the description of the physics of the explosion from the first publication. All lengths measured in feet, yards, and miles, we translated into meters.

0.1 millisecond* the radius of the fiery sphere becomes equal approximately to 14 m, and temperature of its surface is approximately equal to 300,000°K. At this instant illuminance, observable at a distance of 10,000 m, is approximately 100 times more than the illuminance of the surface of earth by the sun.

During the above-described conditions, in the whole volume of the fiery sphere is maintained almost identical temperature; inasmuch as radiant energy can quickly spread between any two points inside the sphere, there is not created considerable temperature gradients. Since the temperature inside the fiery sphere everywhere is identical, it is possible to identify it with an isothermal sphere, which in a given stage is identical with a fiery sphere.

As the fiery sphere expands in air there appears a shock wave; in the beginning the front of the shock wave coincides with the surface of an isothermal sphere. After lowering temperature approximately to 300,000°K speed of shock wave becomes larger than speed of expansion of an isothermal sphere. In other words, transfer of energy by shock wave starts to occur faster than by means of radiation. Nevertheless the luminescent sphere continues to be increased in dimension, inasmuch as strong ecompresion of air, caused by passage of shock wave, causes an increase of temperature sufficient to bring sphere to a glow.

In this stage isothermal sphere is a zone of high temperature inside a fiery sphere, large in dimensions, formed by the sharply outlined front of the shock wave. Interface between the core of this sphere, possessing very high temperature, and the somewhat "colder" air heated by the shock wave, is called the front of radiation.

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*1 millisecond = 10^{-3} sec.

The above-described phenomena are schematically represented in a series of photographs of the fiery sphere (Fig. 9.5), corresponding to different moments of time after an explosion of an atomic bomb; qualitative temperature gradients are shown on the left, gradients of pressure on the right. In the beginning, temperature is identical within the limits of the entire fiery sphere, which at this time is also an isothermal sphere; then there appear two different temperature zones; at this instant the fiery sphere becomes larger than the isothermal sphere remaining inside. The isothermal sphere ceases to be visible since it is covered by the brightly luminescent front of the shock wave. By this moment pressure is increased to maximum, but then already on the surface of the fiery sphere it is sharply lowered, which witnesses to the identity of the fiery sphere with the front of the shock wave.

The fiery sphere continues rapidly to increase in dimensions during approximately 15 milliseconds; during that time its radius attains approximately 90 m, and temperature of surface is lowered approximately to 5000°K, although inside the fiery sphere it is considerably higher. Temperature and pressure of shock wave are lowered so much that the air through which the shock wave passes ceases to gleam. Weakly visible, the front of the shock wave continues to move ahead of the fiery sphere; this phenomenon is called breaking away of the shock wave from the luminescent sphere. Speed of propagation of the shock wave in this period is equal to approximately 4500 m/sec.

In spite of the gradual decrease with time of propagation rate of the front of the shock wave, it always remains larger than speed of expansion of the fiery sphere. In 1 sec the fiery sphere attains

GRAPHIC NOT REPRODUCIBLE

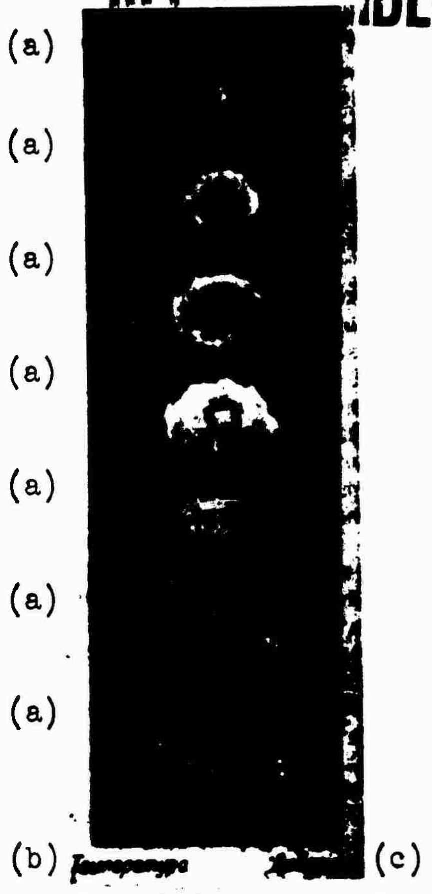

Fig. 9.5. Qualitative picture of the change of temperature and pressure in the fiery sphere. Energy of the explosion is nearly 10^{21} erg ≈ 16 kilograms of uranium ≈ 20,000 m of trotyl.
KEY: (a) Milliseconds; (b) Temperature; (c) Pressure.

its maximum radius of 140 m, and the front of the shock wave by this time goes forward approximately 180 m. In 10 sec, when the fiery sphere rises approximately 450 m, the shock wave departs from place of explosion approximately 3700 m and exceeds the bounds of the zone of its maximum destroying action.

The essential peculiarity of an atomic explosion in air is the special effect which is observed at the time of breakaway of the front of the shock wave from the luminescent sphere. The temperature of the surface of the luminescent region drops approximately to 2000°K and then starts anew to be increased, attaining a second maximum near 7000°K. Minimum temperature is attained approximately 15 milliseconds after explosion, and after approximately 0.3 sec again is increased to maximum. Subsequently there occurs a continuous lowering of the temperature of the fiery sphere due to its expansion and occurring loss of energy.

It is interesting to note that the radiation of the larger part of the radiant energy of an atomic explosion occurs after the brightness of the fiery sphere becomes minimum. Up to this time there is radiated only nearly 1/3 of total energy, in spite of the fact that temperature of surface in this period is very high. This is explained by the fact that the duration of this period 15 milliseconds is extremely small as compared to the time during which radiation occurs after achievement of minimum brightness.

As was mentioned above, the fiery sphere very quickly, less than 1 sec after the explosion, attains a maximum radius of 140 m. Consequently, if the bomb explodes at a height less than 140 m, the fiery sphere should touch the surface of earth; this was observed during the test "Trinity" at Alamogordo (New Mexico).

In view of its small density, the fiery sphere floats upward like a balloon. Several seconds after beginning of motion, speed of sphere attains maximum magnitude, equal to 90 m/sec.

The direct effects of the atomic explosion can be considered completed after approximately 10 sec, when the fiery sphere almost ceases to gleam and the excess pressure of the shock wave decreases to practically safe values.

As was shown earlier, the density of substances inside the fiery sphere is very small since they possess high temperature; therefore, the sphere rises above the place of the explosion of the bomb; as it rises the fiery sphere is cooled. Cooling approximately to 1800°K occurs mainly because of loss of energy due to luminous emittance; then lowering of temperature occurs as a result of adiabatic expansion of gases and mixing of them with ambient air because of turbulent convection. After cessation of glow it is possible to consider the fiery sphere as a great bubble of heated gases, the temperature of which decreases as the "bubble" rises.

The very important distinction between an atomic and an ordinary explosion consists of the fact that in the first case the quantity of liberated energy per unit of mass is immeasurably larger. As a result, there is created a higher temperature, and consequently, a larger part of the energy liberated at the time of the explosion is emitted in the form of luminous emittance. For instance, nearly 1/3 of all energy liberated during an atomic explosion is emitted in the form of luminous emittance. For a nominal atomic bomb this composes approximately $6.7 \cdot 10^{12}$ cal, which is equivalent to $2.8 \cdot 10^{20}$ erg.

The amount of energy passing through the whole spherical surface of the fiery sphere, i.e., through solid angle 4π, is equal to $\sigma T^4 \cdot 4\pi R^2$, where R is radius of sphere, and T is temperature of surface (dependences of R and T on time are shown in Fig. 9.6). Inasmuch as into the air penetrates only part of energy f_0,* the quantity of radiant energy reaching all points on a spherical surface located at a moderate distance from point of explosion will be equal to $f_0 \sigma T^4 \cdot 4\pi R^2$. Hence flux of radiant energy φ per unit of area at distance D is obtained by means of dividing this expression by surface area of sphere $4\pi D^2$, i.e.,

$$\varphi = f_0 \sigma T^4 \left(\frac{R}{D}\right)^2.$$

From this formula it is possible to calculate flux of radiant energy at a given point at distance D for different moments of time after an atomic explosion, using values R and T from Fig. 9.6, and f_0 from Fig. 9.7. In order not to construct curve for different distances, magnitude φD^2, equal to $f_0 \sigma T^4 R^2$, is given in Fig. 9.8 as a function of time; energy flow is measured in cal/cm^2·sec and distance in m. By the curve it is possible to easily determine energy flow at any given distance at any moment.

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*It is considered that air passes only wave lengths exceeding $\lambda_0 = 1860$ Å so that f_0 is the fraction of energy of Planckian spectrum of temperature T, included in the wave length range from $\lambda_0 = 1860$ Å to $\lambda = \infty$. Function f_0 (T) is shown in Fig. 9.7.

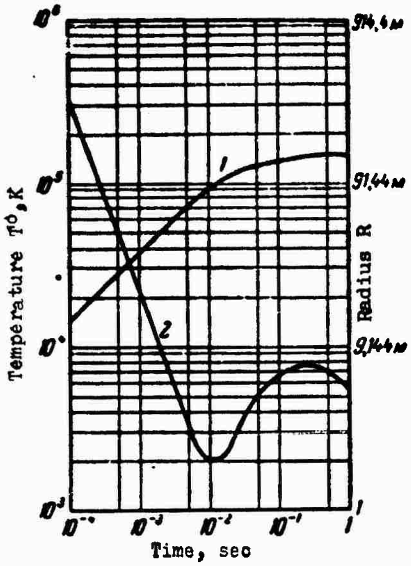

Fig. 9.6. Dependence of radius of the fiery sphere (curve 1) and temperature (curve 2) on time, starting from the moment of explosion.

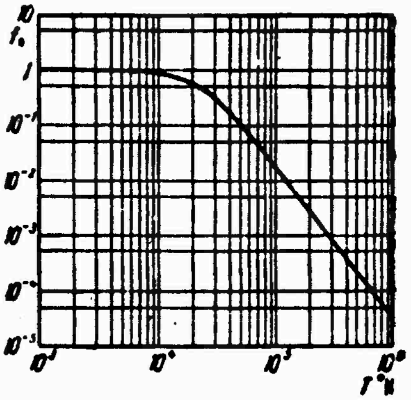

Fig. 9.7. The fraction of equilibrium radiation included in wave length range from λ = 1860 Å to λ = ∞ depending upon temperature

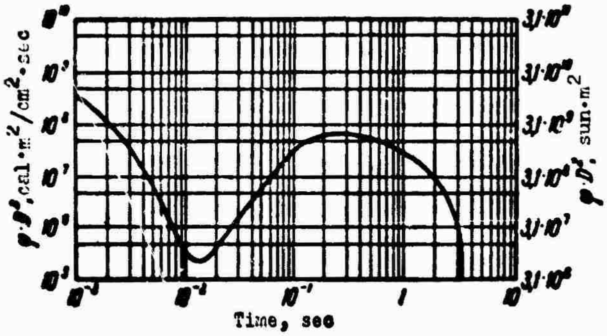

Fig. 9.8. Dependence of energy flow emitted by the fiery sphere on time past after the explosion.

In order to obtain some idea about the magnitude of illuminance it is expedient to introduce the unit "sun," which is defined as energy flow equal to 0.032 cal/cm^{2}sec and is assumed equal to solar energy incident on the upper boundary of the atmosphere. The right ordinate in Fig. 9.8 gives value φD^2, where φ is expressed in suns, and D in meters.

During minimum brightness, magnitude of φD^2 is equal approximately to $6.8 \cdot 10^6$ sun·m^2, so that at this instant the fiery sphere, observed at a distance of 2600 m, should seem approximately as bright as the sun. In reality it will be somewhat less bright depending upon cleanness of air, and also due to absorption of radiation in the atmosphere."

On this we finish the description borrowed from the book [11].

As long as the front of the shock wave does not break away from the boundary of the luminescent body and the latter simple coincides with the front of the shock wave, the law of propagation of the fiery sphere is very well described by formula $R \sim t^{2/5}$, which follows from the solution of the problem about strong explosion, considered in § 25, Chapter I. By the moment of breakaway, temperature on the front of the shock wave is equal to approximately 2000°K, which corresponds to a pressure of $p_f \approx 50$ atm. This pressure is considerably higher than atmospheric, i.e., initial assumptions lying in the basis of solution $(p_f \gg p_0)$, are executed.

Comparison of theoretical law $R \sim t^{2/5}$ with experimental data is done in the book of L. I. Sedov [13].

In the book is plotted a graph of straight line 5/2 log R depending upon log t, on which are marked experimental points relating to the explosion of the atomic bomb in New Mexico in 1945. Experimental points lie very well on a theoretical straight line. According to formula (1.110) slope of the straight line is connected with energy of explosion E:

$$R = [\alpha\,(\gamma)\,\frac{E}{\rho_0}]^{1/5} t^{2/5};\quad 5/2 \log R = \frac{1}{2} \log (\alpha \frac{E}{P} \qquad) \alpha \frac{E}{\rho_0} + \log t.$$

Here $\alpha = \xi_0^5$, where ξ_0 is coefficient in formula (1.110).

During air density $\rho_0 = 1.25 \cdot 10^{-3}$ g/cm^3 magnitude of αE is obtained equal to $8.45 \cdot 10^{20}$ erg. Dependence of coefficient α on adiabatic index γ is presented in the book of L. I. Sedov [13].

If one were to assume $\gamma = 1.4$, as L. I. Sedov did, then $\alpha = 1.175$ and $E = 7.19 \cdot 10^{20}$ erg. In reality, the effective adiabatic index is somewhat less since at high temperature air is strongly dissociated and ionized; coefficient α with this is larger and energy of explosion turns out to be smaller. Thus, for instance, if one were to take $\gamma = 1.32$, there is obtained $\alpha = 1.3$ and $E = 6.5 \cdot 10^{20}$ erg.

§ 6. Breaking Away of the Front of a Shock Wave from the Boundary of the Fiery Sphere

We will observe what the nature of the glow of the fiery sphere is at temperatures after the front of the shock wave of an order of several thousands of degrees, and we will clarify the causes of the phenomena of breakaway of a front of a shock wave from the boundary of a luminescent body and the minimum brightness of the fiery sphere. These questions were considered in the works of one of the authors [14, 15].

In the absorption (and emission) of visible light in heated air there participates a whole series of mechanisms: the photoionization of highly excited atoms and molecules of oxygen and nitrogen and molecules of nitric oxide, the knocking out of weakly bound electrons from negative ions of oxygen, the molecular absorption (without breakaway of electrons) by molecules of O_2, N_2, NO remaining in excited states, and finally, the molecular absorption by molecules of NO_2 present in small quantity in heated air. Coefficients of absorption, connected with all these mechanisms, were estimated in Chapter V. The comparative role of different mechanisms of absorption and the absolute value of coefficients strongly change depending upon temperature and air density. At temperatures higher than ~ 12,000-15,000°K basically there occurs photoionization of molecules and atoms of oxygen and nitrogen. During air density approximately 10 times more than normal, which takes place after the front of a shock wave, and temperatures ~ 12,000-15,000°K the mean free path of visible quanta turns out to be of the order of millimeters. The mean free path sharply decreases during temperature increase.

In the region of lower temperatures, ~8000-6000°K, on the first plan there sets in photoionization of NO molecules, absorption by negative ions of oxygen, and molecular absorption by molecules of O_2, N_2, and NO. The mean free paths of visible light in this interval of temperatures also strongly depend on temperature and have an order of 10-100 cm (during tenfold compression in the shock wave). At still lower temperatures, lower than ~5000°K, all mechanisms lead to extraordinarily weak absorption rapidly decreasing with lowering of temperature. Practically the only mechanism of absorption of visible light in air at $T < 5000°K$ is absorption by molecules of nitrogen peroxide NO_2. In spite of the small concentration, nitrogen peroxide rather strongly absorbs visible light, ensuring mean free paths measured in meters. Thus, at a temperature of $T = 3000°K$ and density five times more than normal, concentration of dioxide is equal to $c_{NO_2} = 1.6 \cdot 10^{-4}$,* and the mean free path of red light, calculated with absorption cross section $\sigma_{NO_2} = 2.15 \times 10^{-19}$ cm^2, is $l_\nu = 220$ cm.

It is known that after the front of the shock wave of a strong explosion, temperature increases from front to center (see § 25, Chapter I). If one were to consider that stage of explosion when the temperature on the front is equal to several thousand degrees, then during nominal energy of explosion $E = 10^{21}$ erg (corresponding approximately to 20,000 m of trotyl) the blast wave embraces a sphere with a radius of the order of hundreds of meters, and temperature after the front noticeably increases during removal from front to center at a distance of the order of meters.

In this stage radiant heating of air before the shock discontinuity and shielding of the surface of the front, considered in § 1 and 3,

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*Concentration c_i is defined as the ratio of the number of i-th particles to the initial number of molecules in cold air.

temperatures lower than ~2000°K time, necessary for the formation of any noticeable quantity of oxide, it turns out to be extraordinarily large as compared to the time of existence of heated particles in the shock wave, and reaction does not manage to occur.

Thus, in layers of air heated by the front of the shock wave to a temperature lower than ~2000°K, nitrogen peroxide, the only absorbing agent, will never be formed; these layers are absolutely transparent for visible light and by themselves do not gleam.

At the time when temperature on the front T_f is less than 2000°K, we will say when $T_f = 1000°K$, from afar will be seen a luminescent disk, the radius of which is less than the radius of the front of the shock wave. The horizontal section of the blast wave is depicted in Fig. 9.9. Beams of type B intersect layers of air heated by the shock wave to a temperature lower than ~2000°K and, therefore, nonluminous.

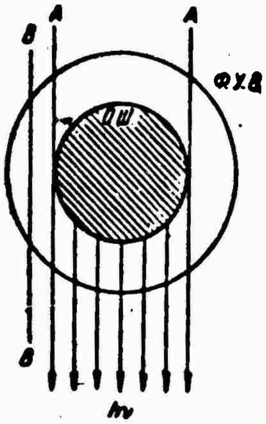

Fig. 9.9. Diagram of the glow of a fiery sphere after breakaway. Internal circle — O. Sh. — is the boundary of the luminescent body, the fiery sphere; external circle — F. U. V. — is the front of the shock wave.

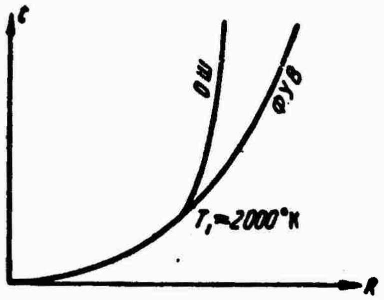

Fig. 9.10. Lines of front of shock wave (F. U. V.) and boundary of fiery sphere (O. Sh.) on diagram R, t.

The fiery sphere is limited by beams A going out from center O exactly to distance $R_{O.Sh.}$, corresponding to the radius of those layers of air at a given moment, which earlier were heated by the front to a temperature of ~2000°K and in which a quantity of nitrogen peroxide is necessary for a noticeable flow. Inasmuch as particles of air in the blast wave scatter from the center (actually, more slowly than the front itself moves), the radius of the fiery sphere $R_{0.Sh.}$ is increased. The fiery sphere is expanded as long as pressure in the blast wave does not drop to atmospheric and motion does not cease.* The nonluminous front of the shock wave, detaching from the fiery sphere when the temperature on it is ~2000°K, departs far forward. (The trajectory of the front and the fiery sphere are schematically depicted in Fig. 9.10).

§ 7. The Effect of Minimum Brightness of the Fiery Sphere

We will observe how, with the passage of time, brightness and effective temperature of the surface of the fiery sphere change in the stage of breakaway of the shock wave from the boundary of the luminescent body. When temperature of the front drops below ~5000°K, the mean free path of visible light grows to a magnitude of the order of a meter and the fiery sphere ceases to radiate as an ideal black body. The effective temperature in these conditions one should calculate by the general formula (2.52) in accordance with distributions of temperature and coefficient of absorption along the radius after

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*During adiabatic expansion to atmospheric pressure of particles of air with initial temperature $T_f \approx 2000°K$ corresponding to pressure on front $p_f \approx 50$ atm, particles cool to $T \sim 800°K$. Probably, with the passage of time the boundary of the luminescent region somewhat shifts deep into layers with temperatures closer to 2000°K, since radiating ability proportional to $\exp(-h\nu/kT)$, very rapidly decreases with lowering of temperature even during constant coefficient of absorption ($h\nu \gg kT$ at $h\nu \approx 2$ ev, $T \sim 2000-1000°K$). More exactly, the boundary of the fiery sphere is determined by the sensitivity of the recording instrument.

the front of the waves.*

We will consider, for example, moment of time $t = 1.5 \cdot 10^{-2}$ sec when radius of the front is R = 107 m and temperature on front is $T_f = 3000°K$ (all calculations pertain to an explosion with energy $E = 10^{21}$ erg). In Fig. 9.11 is shown the distribution of the coefficient of absorption of red light $\lambda = 6500$ Å along the radius after the front of a shock wave (coordinate x is counted off from the front to the depth of the sphere). In the same place are shown temperature and relative air densities (compression $\eta = \rho/\rho_0$) at several points. Distributions of temperature and density after the front are taken from the solution of the problem about a strong explosion; concentrations of nitrogen peroxide were calculated as presented in § 5, Chapter VIII.

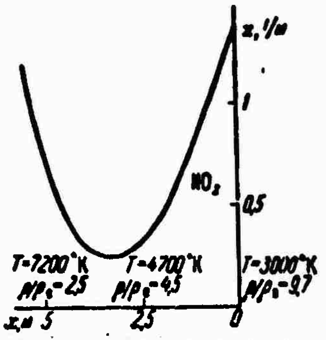

Fig. 9.11. Distribution of the absorption of red light after the front of a shock wave at a temperature of $T_f = 3000°K$ for an explosion with $E = 10^{21}$ erg. There are shown values of temperatures and densities at several points. Adiabatic index $\gamma = 1.23$.

Inasmuch as the exact values of the effective absorption cross sections of red light by excited molecules of NO_2 are unknown, for tentative calculations were accepted the following, apparently, probable values of sections (see § 21, Chapter V):

T, °K	4000	3000	2600	2000
$\sigma_{NO_2}\,10^{19}$, см^2	3,0	2,15	1,8	0,84

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*Radiating layer has a thickness of the order of tens of meters, which is considerably less than the radius of the sphere $R_{0.Sh.} \sim 100$ m. Therefore, curvature of the layer it is possible to disregard and to consider it flat, i.e., to use formula (2.52). Let us note that formula (2.52), into which enters integral exponential, appearing as a result of the calculation of slanting rays, gives a luminance temperature averaged over the disk. If one were to be interested by the brightness

From Fig. 9.11 it is clear that at temperatures higher than 6000-7000°K, absorption connected with the many mechanisms enumerated above grows very greatly and rapidly during removal from the front, when temperature is increased. In region $T \sim 6000°K$ absorption weakens and passes through minimum, since with such temperature all these mechanisms give very small coefficient, but concentration of dioxide is still small (equilibrium of reaction $NO + \frac{1}{2} O_2 \rightleftarrows NO_2$ at such high temperatures is shifted to the side of disintegration of dioxide). Concentration of dioxide increases at lower temperatures ~4000-3000°K, which also leads to increase of absorbing ability near front of wave.

Essentially, layers of air with temperatures higher than ~6000-7000°K turn out to be absolutely opaque and from internal "hot" sphere with such a temperature on the surface there emerges outside a flux of Planck radiation. External layer of air, containing dioxide, plays a double role. On the one hand, it absorbs this high-temperature radiation, outgoing from surface of "hot" sphere, but on the other hand it radiates light itself. Formally it is possible to describe this position by breaking down the integral with respect to τ_ν in formula (2.51) into two parts: one with respect to external layer of dioxide with optical thickness τ_ν^*, and the other with respect to internal "hot" region $\tau_\nu^* < \tau_\nu < \infty$:

$$S_\nu(T_{эф}) = 2\int_0^\infty S_{\nu p} E_2(\tau_\nu)\, d\tau_\nu = 2\int_0^{\tau_\nu^*} S_{\nu p} E_2(\tau_\nu)\, d\tau_\nu + 2\int_{\tau_\nu^*}^\infty S_{\nu p} E_2(\tau_\nu)\, d\tau_\nu.$$

[FOOTNOTE CONT'D FROM PRECEDING PAGE].
in the center of the disk, then instead of integral exponential $E_2(\tau_\nu)$ one should write usual $\exp(-\tau_\nu)$, where τ_ν is optical thickness, counted off along the radius from the surface of the front to the depth of the sphere. Subsequently, there is calculated average luminance temperature.

In distinction from formula (2.51) we here, instead of density of radiation, write flux, which is all the same.

In the second integral it is possible to carry out certain mean value $S^*_{\nu p}$, corresponding to effective temperature of "hot" sphere T^* ($T^* \sim 7000^\circ K$), and, using properties of integral exponentials, to record:

$$S_\nu(T_{\text{эф}}) = 2\int_0^{\tau_\nu^*} S_{\nu p}E_2(\tau_\nu)\,d\tau_\nu + S_{\nu p}(T^*)\,E_3(\tau_\nu^*).$$

The first member gives intrinsic emission of layer of dioxide, and in the second, factor E_3 (τ^*_ν) considers the shielding by this layer of "high-temperature" radiation of "hot" sphere. Calculations show that with passage of time the relative role of the second member increases, and intrinsic radiation of dioxide becomes small, i.e., the role of dioxide leads basically to shielding of high-temperature radiation. In considered example $T_f = 3000^\circ K$ optical thickness of layer of dioxide $\tau^*_\nu = 2.42$, and effective temperature of fiery sphere is equal to $T_{ef} = 4110^\circ K$.

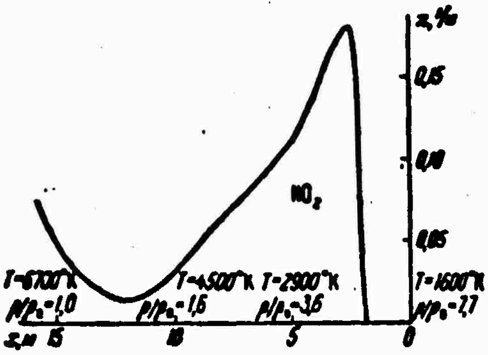

Fig. 9.12. Distribution of absorption of red light after front of shock wave at a temperature on front of $T_f = 1600^\circ K$ for explosion with $E = 10^{21}$ erg. There are shown values of temperatures and densities at several points. Adiabatic index $\gamma = 1.30$.

Another typical picture of distribution of coefficient of absorption along the radius appears when temperature on front of shock wave drops lower than $2000^\circ K$. Absorption starts not at once after front but somewhat deeper, since in layers close to front and heated during passage of front to a temperature lower than $2000^\circ K$, dioxide is lacking, and these layers do not absorb light. Such a picture is depicted in Fig. 9.12 ($t = 2.64 \cdot 10^{-2}$ sec, $R = 138$ m, $T_f = 1600^{\circ}$K).

Let us trace how effective temperature of radiation changes with the passage of time. While temperature on front of shock wave is higher than $\sim 2000^{\circ}$K, in layers of air again seized by the front will be formed dioxide; full optical thickness of layer of dioxide increases and brightness drops. Luminance temperature at $T_f \lesssim 5000^{\circ}$K exceeds temperature of front, since layer of dioxide does not completely shield high-temperature radiation (with $T^* \sim 7000^{\circ}$K), proceeding from depth. When temperature of front becomes lower than 2000°K, in layers of air seized again, dioxide no longer will be formed. Even if full quantity of molecules NO_2, available by this moment in air, remained constant, optical thickness of shielding layer of dioxide, all the same, would decrease with passage of time, since due to scattering of air the same number of molecules NO_2 would be distributed along spherical layer of a larger and larger radius. It is easy to see that optical thickness of layer of dioxide is

$$\tau_\nu^* = \int_0^R n_{NO_2} \sigma_{NO_2} \, dr,$$

where n_{NO_2}, number of molecules NO_2 in 1 cm^3, decreases during constant full number

$$N_{NO_2} = \int_0^R 4\pi r^2 n_{NO_2} \, dr \approx 4\pi R^2 \int_0^R n_{NO_2} \, dr,$$

roughly speaking, it is proportional to $R^{-2} \sim t^{-4/3}$.

In reality, full quantity of dioxide, after its formation ceases, even somewhat drops due to disintegration of molecules NO_2 (see § 5, Chapter VIII), which leads to a still faster fall of optical thickness τ_ν^*.

Thus, starting from the moment when temperature on front becomes less than ~2000°K, shielding by layer of dioxide decreases and gradually internal hot region is "bared." Effective temperature of fiery sphere, passing through minimum, is increased; sphere, as it were, again inflames, which is observed by experiment.

The presented concepts about the nature of minimum brightness are illustrated in Table 9.4, in which are presented results of calculation of effective temperatures for explosion with energy of $E = 10^{21}$ erg. T_{ef} passes through minimum equal to 3600°K, and τ_{ν}^{*} passes through maximum at a temperature of front $T_f = 2600$°K, close to temperature of breakaway $T_f = 2000$°K.

It is interesting to trace what occurs with minimum of brightness during transition from one energy of explosion to another. All times and dimensions in a strong blast wave are changed similarly, proportionally to $E^{1/3}$ (thanks to approximate accuracy of self-simulating solution of problem about a strong explosion). Roughly speaking, optical thicknesses at corresponding moments of time (during identical temperature of front), also change as $E^{1/3}$ (since concentration of dioxide in basic region is equilibrium and depends mainly on temperature and density of particle, but not on time of existence of it in a heated state). It follows from this that shielding by layer of dioxide decreases with decrease of energy of explosion, but excess of T_{ef} over T_f increases: minimum becomes less deep. As an example in Table 9.4 are given results of calculation T_{ef} (T_f) for energy of explosion $E = 10^{20}$ erg. Position of minimum was not changed, and minimum brightness became higher: $T_{ef\ min} \approx 4800$°K.

In the limit of very small energies of explosion minimum should, in general, disappear. Conversely, in the limit of very high energies of explosion all dimensions and optical thicknesses become large; radiation of fiery sphere more and more nears radiation of black body and T_{ef} nears T_f until the moment when T_f becomes equal approximately to 2000° K, i.e., minimum becomes deeper $T_{ef\ min} \approx 2000^\circ K$. Lower than 2000°K luminance temperature is not able to fall since even during very high energies of explosion and long times of process, dioxide, all the same, will not be formed at $T < 2000^\circ K$, and air heated in shock wave to temperature $T_f < 2000^\circ K$ is transparent and does not radiate.

Table 9.4. Calculated in Work [15], Values of Luminance Temperature of a Fiery Sphere in Red Light $\lambda = 6500$ Å in the Stage of Minimum of Brightness.

$t \cdot 10^2$ sec	R, m	T_f K	T_{ef} °K	τ_v^0
		$E = 10^{21}$ erg		
0,75	82	5000	5930	1,06
1,05	93	4000	4810	1,96
1,50	107	3000	4110	2,42
1,81	109	2600	3600	3,23
1,95	112	2300	4150	2,16
2,25	128	2000	4520	1,80
2,39	132	1800	4810	1,61
2,64	138	1600	5400	1,15
2,94	143	1400	5600	1,11
		$E = 10^{20}$ erg		
0,43	40	5000	6380	0,61
0,61	53	4000	5560	1,16
0,72	58	3000	5000	1,42
0,82	60	2600	4800	1,77
0,95	65	2300	5390	1,18
1,01	66	2000	5850	0,96
1,16	70	1800	6050	0,88
1,38	73	1600	6510	0,71
1,41	75	1400	6980	0,54

§ 8. Cooling of Air by Radiation

We will present that gas-dynamic process during strong explosion in air with energy $E \sim 10^{21}$ erg occurs adiabatically, as is described in § 25, Chapter I. Scattering of air enveloped by blast wave is strongly delayed until the moment when pressure in it drops to a magnitude of the order of atmospheric. Subsequently shock wave gradually weakens, is turned into acoustic and removes with itself far forward a large fraction of total energy of explosion. In central regions after achievement of atmospheric pressure and cessation of motion there remains a large mass of air, irreversibly heated by the shock wave. In it is concentrated "residual" energy of explosion, which composes a very considerable (of the order of tens of percents) fraction of total energy of explosion. The air turns out to be heated to very high temperatures. Thus, for instance, layers of air through which front of shock wave passed with amplitude $p_f = 750$ atm heating them to temperature $T_f = 11{,}000^\circ$K, after expansion to atmospheric pressure remain heated to temperature of the order of 2000°K.*

The layers closer to center, initially heated by front of shock wave to several hundreds of thousands of degrees (pressure on front of the order of hundreds of thousands of atmospheres), remain heated to tens of thousands degrees, etc.

Thus, after explosion will be formed huge volume of air with radius of the order of hundreds of meters, heated to high temperatures. In central regions temperature attains hundreds of thousands of degrees; toward periphery it gradually drops to thousand degrees and lower, to standard atmosphere temperature.

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*Residual temperature, roughly speaking, is equal to $T_{res} \approx T_f$ $(1 \text{ atm}/p_f \text{ atm})^{(\gamma-1)/\gamma}$. For appraisal it is possible to take effective value of adiabatic index $\gamma \approx 1.3$.

Let us set up the question: what is further fate of residual energy of air, irreversibly heated by blast wave, and how does this air cool? This question was considered in works of A. S. Kompaneyets and authors [16, 17].

It is clear that resorption of energy by means of molecular thermal conduction does not play a role. During coefficient of diffusion of heat (temperature transfer) of air of the order of 1 cm^2/sec volume with radius of $\sim 10^4$ cm would cool in a year. Convection rise of heated sphere because of difference in densities of cold and hot air at identical atmospheric pressure and (connected with the rise) the mixing of hot gas with surrounding masses of cold are more essential. However, in the first 2-3 sec after explosion rise is small. Rise cannot exceed magnitude of $gt^2/2$, where g is acceleration due to gravity, which composes 5 m for 1 sec, 20 m for 2 sec, and 45 m for 3 sec. Therefore, being interested in the first several seconds after the moment of explosion, it is possible not to consider convection.

The basic process leading to cooling of air and energy dissipation of irreversible heating in space is luminous emittance. Actual possibility of radiant cooling is a corollary of the fact that cold air is transparent in a certain spectrum "window": in the visible part of the spectrum and adjacent regions of ultraviolet and infrared radiation. Thanks to the existence of just such a "window" of transparency, corresponding quanta, radiated by heated gas, can freely depart to great distances, removing with themselves energy from the heated volume.

A characteristic peculiarity of the process of de-excitation of energy from heated air is its non-stationary nature. In this respect there is a fundamental distinction from the similar, at first glance, process of radiation of stars (in particular the sun, feeding by illuminated energy our planet). In stars the loss of energy because of radiation from the surface is compensated by flow of energy from within, liberated due to nuclear reactions occurring in central parts (see Chapter II, § 14). As a result conditions are established, in which each element of volume obtains as much radiant energy as it emits, and distribution of temperature along the radius of a star has an established, stationary (during the period of visible times) character.

In the considered case there are no sources of energy; initial distribution of temperature is determined by the preceding history of the phenomenon and by the gas dynamics of the process of propagation of a blast wave, and the air gradually cools because of the fact that energy is carried away by radiation.

Our problem consists of clarifying how the process of cooling takes place, how temperature changes at different places in the heated volume and, finally, the most essential, what are the radiant cooling rate and the radiation flux from the surface of a heated body.

§ 9. Appearance of Temperature Step — Cooling Wave

The basic factor determining uniqueness of the process is the extremely sharp temperature dependence of transparency of air, about which we have already spoken repeatedly above. If we consider temperature dependence of the mean free path of certain radiation averaged over the spectrum, characteristic for a given temperature, let us say, the mean free path of quanta $h\nu$, 3-5 times exceeding kT,* and to consider that during constant pressure, close to atmospheric, air

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*We are reminded that maximum of Planck spectrum with respect to frequency was apportioned to quanta $h\nu = 2.8$ kT; maximum of weighing function during Rosseland method of averaging mean free path lies in the region $h\nu \approx 4$kT.

density decreases with growth of its temperature, then we will come to the following conclusions. The mean free path of quanta changes from kilometers at temperatures of the order of $6000^\circ K$ to a hundred meters at $T \sim 8000^\circ K$, tens of meters at $T \sim 10,000^\circ K$, and ten centimeters at $T \sim 15,000^\circ K$.

Obviously, radiation flux outgoing from the heated volume with smooth distribution of temperature is determined by the temperature of that layer (radiating) in which the mean free path has the order of characteristic dimensions of the problem, the order of ten meters. External, less heated layers are transparent and by themselves virtually do not radiate light. The deeper ones are opaque and quanta generated in them are not in a state to depart a considerable distance. We have already encountered such a position when examining radiation of heated zone of air before discontinuity in a very strong shock wave. By analogy it is possible also to introduce into this problem the idea of transparency temperature T_2, as such a temperature at which the mean free path of light has the order of characteristic distance where temperature noticeably changes. In distinction from the problem about glow of heated layer, where dimensions were 10^{-2}-10^{-1} cm and temperature of transparency $\sim 20,000^\circ K$, here scale is of the order of 10 meters and temperature of transparency $T_2 \sim 10,000^\circ K$.

We will present now a spherical volume of motionless air with smooth (at initial moment) distribution of temperature, changing along radius from $\sim 100,000^\circ K$ in the center to several thousand degrees on the periphery, and we will see how this distribution changes with the passage of time (we will disregard motion of air, which could appear because of gradients of pressure).

In accordance with the above said, it is possible to expect that the layer begins to radiate and to be cooled with a temperature of the order of transparency temperature ($T_2 \sim 10{,}000^{\circ}K$); at the following moment in smooth (in the beginning) distribution of temperature there will be formed a "recess", as shown in Fig. 9.13. Subsequently this "recess" obtains the form of a temperature step, which spreads to the depth of the heated sphere, to the center. One after another layers of air are cooled from initial temperature to a temperature of the order of 10,000°K, after which they become transparent and practically cease to radiate. Internal layers hardly change their temperature until they approach a step, since in these layers the mean free path of light is very small, and emitted quanta right here are absorbed inversely.

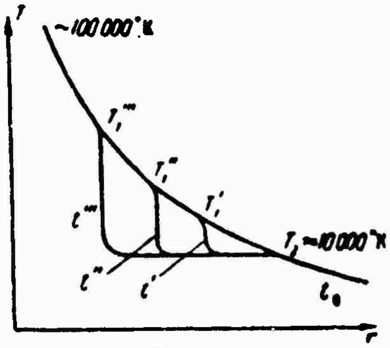

Fig. 9.13. Appearance of step (wave of cooling) from continuous distribution of temperature and its propagation in air at rest; $t_0 < t' < t'' < t'''$.

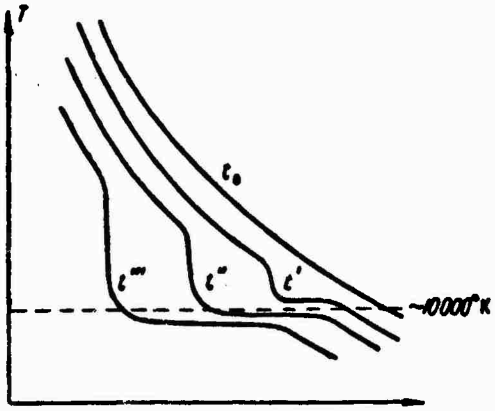

Fig. 9.14. Appearance and propagation of wave of cooling in scattering and adibatically cooled air; $t_0 < t' < t'' < t'''$.

Thus, air is cooled as a result of propagation by it of some kind of narrow temperature step, which it is possible to call "wave of cooling." Temperature in wave of cooling sharply (as compared to initial smooth distribution) drops from initial value T_1, equal to temperature in that place toward which at a given moment the upper boundary of the wave approached, to a lower value — the temperature of transparency T_2 at which air practically ceases to radiate.

Depicting consecutive changes of distribution of temperature in Fig. 9.13, we were distracted from change of temperature because of gas-dynamic motion, considering air to be motionless. In reality step will be formed until air pressure drops to atmospheric and motion is ceased, and namely, when speed of cooling by radiation of layer with temperature $\sim 10{,}000^{\circ}K$ becomes comparable with speed of adiabatic cooling connected with scattering and expansion of air in blast wave. In the earlier stage of explosion speed of adiabatic cooling is great, and air does not manage to de-excite its energies, since region of temperatures $\sim 10{,}000^{\circ}K$ at which step could be formed is "skipped" very fast and air becomes transparent, never managing to lose noticeable energy content on radiation. Subsequently, when adiabatic cooling decreases as pressure falls and scattering declerates, in the first plan there sets in cooling by radiation. Appraisals show that during explosion with energy $E = 10^{21}$ erg the step after the front of the shock wave starts to be revealed in layer with $T \sim 10{,}000^{\circ}K$ at time $t \sim 10^{-2}$ sec when temperature on the front is of the order of $2000^{\circ}K$ and pressure is of the order of 50 atm (pressure in a blast wave little changes from front to center, see § 25, Chapter I).

Taking into account adiabatic cooling, the picture of distributions of temperature in air through which spreads wave of cooling is depicted in Fig. 9.14. Along the axis of abscissas there is located not a Euler but a Lagrange coordinate, i.e., Fig. 9.14 shows how temperature of given particles of air changes and how a cooling wave spreads not through space but through a "mass" of gas.

§ 10. Energy Balance and Speed of Propagation of a Cooling Wave

Wave of cooling runs through air practically undisturbed by radiation. Temperature of gas by the moment of approach of upper boundary of step is determined only by preceding history of the process and hydrodynamic motion (if such exists). This is explained by the fact that at temperatures of the order of tens of thousands of degrees and gradients of temperature of the order of a thousand degrees per meter, which take place in initial distribution, radiant thermal conduction is too small to create any noticeable energy flow in opaque region to which the wave of cooling still has not come. Radiant thermal conduction, coefficient of which is proportional to Rosseland mean free path l (T) and cube of temperature,* fast increases with increase of temperature and becomes essential only in the region of temperatures of the order of hundreds of thousands of degrees, near the center of the explosion. It limits rise of temperature in the center by a magnitude of such an order and levels temperature near the center.

Coefficient of thermal conduction becomes again large in region of temperatures lower than 10,000°K, where mean free path, sharply increasing with decrease of temperature, becomes very great.** However, this does not mean that at low temperatures radiant thermal conduction also levels temperature, since in this region heated air becomes

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*We are reminded that energy flow, transferable by means of radiant thermal conduction, $S = -\varkappa\, \partial T/\partial r$, where coefficient of radiant thermal conduction is $\varkappa = 16\sigma l\ (T)T^3/3$ (see § 12, Chapter II).

**$l(T)$ passes through minimum at $T \sim 50{,}000^\circ K$, and coefficient of radiant thermal conduction, proportional to $l(T)T^3$, at $T \sim 10{,}000^\circ K$.

transparent and the idea of thermal conduction, in general, loses its meaning — transfer of radiation obtains essentially another character, in particular, leading to the formation of a wave of cooling.

Thus, thanks to small thermal conduction on upper edge of wave of cooling, energy flow of radiation, proceeding in the wave from within, is close to zero and cannot influence properties of the wave. The entire radiation flux, discharging energy of particles of air which are cooled in the wave, is generated inside the actual wave. Definition of this flux, which we will designate S_2, composes a basic problem of theory (to the solution of it will be dedicated § 3 of this Chapter). This problem is nontrivial since inside the wave is a very sharp distribution of temperature. It is clear only that flux is included in limits of $\sigma T_1^4 > S_2 > \sigma T_2^4$ since radiating layer in the wave lies at temperatures lower than the upper T_1, at which air is absolutely opaque, but above lower T_2, lower than which air is transparent; it does not radiate and is not cooled because of de-excitation of energy.

If flux S_2 is known, then speed u of propagation of wave of cooling through mass, on which in the end depends time of cooling of heated volume, can be found from condition of energy balance. The fact is that, according to appraisals, the wave of cooling spreads along air undisturbed by radiation with a speed less than the speed of sound. Pressure during the extent of the thin layer — the "front" of the wave — manages to level out and turns out to be practically constant. Density of gas is automatically "tuned" to change of temperature so that, while passing through wave and being cooled, a particle of air is compressed proportionally to 1/T (if it is considered that pressure $p \sim \rho T$). This is illustrated in Fig. 9.15.

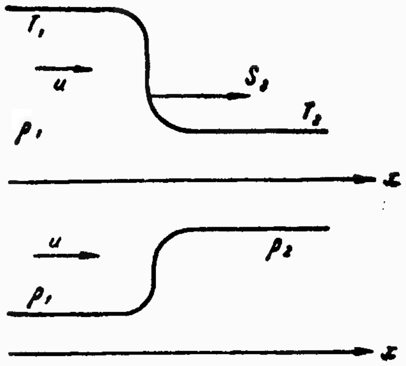

Fig. 9.15. Schematic illustration of profiles of temperature and density of gas i[illegible]e front of a cooling wave. Pointer u shows direction of airspeed, flowing in wave.

Process of cooling air in the wave occurs at constant pressure. If ρ_1 is initial air density at the time of the approach of the wave, then quantity of air flowing through 1 cm^2 of surface of front in 1 sec is equal to $\rho_1 u$. Change of its energy during cooling from temperature T_1 to T_2 is (during constant heat capacity) $\rho_1 u c_p (T_1 - T_2)$. This change is equal, obviously, to the energy drawn off from the surface of the front of the wave by radiation, i.e., equal to flux S_2.

Thus, we obtain the fundamental equation of energy balance on a wave of cooling, which we consider here as a discontinuity:

$$S_2 = \rho_1 u c_p (T_1 - T_2). \qquad (9.5)$$

If we consider that heat capacity c_p is not constant, then we will obtain more general equation:

$$S_2 = \rho_1 u (w_1 - w_2), \qquad (9.6)$$

where w is specific enthalpy of air.

If γ is effective adiabatic index, then $w = \frac{\gamma}{\gamma - 1} \frac{p}{\rho}$ and speed of wave is equal to

$$u = S_2 \frac{\gamma - 1}{\gamma} \frac{1}{p} \left(1 - \frac{w_2}{w_1}\right). \qquad (9.7)$$

In the third section of the chapter it will be shown that radiation, outgoing from the surface of the wave of cooling, always is generated on the lower edge of the step, independently of "amplitude" of wave, which it is possible to characterize by ratio T_1/T_2 or w_1/w_2, i.e., during any amount of high temperatures of initial gas T_1, temperature of outgoing radiation is close to T_2.

Flow value S_2 is determined basically by temperature of transparency and approximately is equal to

$$S_2 = 2\sigma T_2^4. \tag{9.8}$$

Actual temperature of transparency is not a magnitude strictly defined. As was already mentioned above, it tentatively differentiates transparent and opaque temperature ranges and is found from the condition that average (over the spectrum) mean free path of radiation at a temperature equal to the temperature of transparency is of the order of characteristic scale of problem d, for instance the distance at which temperature of air drops from T_2 to a sufficiently small magnitude, let us say, 2000°K.

Table 9.5. u, km/sec at p = 1 atm

T_1°K / T_2°K	10700	9700	9300
20 000	2,7	2,1	1,7
50 000	1,8	1,4	1,1
100 000	1,6	1,2	1,0

When wave spreads along expanded air, this scale is determined by hydrodynamic of the process on the whole; it is less the larger the speed of adiabatic cooling. If one were to approximately describe coefficient of absorption of air by Boltzmann dependence $\varkappa \sim \exp(-I/kT)$ with a certain effective value of "ionization potential,"* then temperature of transparency turns out to be only weakly, logarithmically depending on scale d, just as on air density, which enters only into pre-exponential factor:

$$l(T_2) = \text{const}\, e^{\frac{I}{kT_2}} = d; \quad T_2 = \frac{I}{k}\left(\ln\frac{d}{\text{const}}\right)^{-1}. \tag{9.9}$$

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*In reality, $\varkappa$ is the sum of members of type $e^{-I/kT}$, where I is ionization potential for components corresponding to photoelectric absorption, and excitation energy for components of molecular absorption. All values of I are of the order of 5-10 ev; if one were to consider a not very great temperature range, then always it is possible to interpolate $\varkappa(T)$ by dependence of the type $\exp(-I/kT)$.

Above it has already been said that $T_2 \sim 10{,}000^\circ K$ at $d \sim 10$ m and atmospheric pressure (at $d \sim 100$ m $T_2 \sim 8000^\circ K$; at $d \sim 1$ m $T_2 \sim \sim 12{,}000^\circ K$). Thus, flow value $S_2 = 2\sigma T_2^4$ changes in rather narrow limits and, if we consider strong waves of cooling with large temperature gradient ($T_1 \gg T_2$, $w_1 \gg w_2$), then it will appear that speed of propagation of wave along initial gas depends basically only on pressure of gas p, independently of upper temperature T_1:

$$u \approx S_2 \frac{\gamma-1}{\gamma} \frac{1}{p} \quad \text{at} \quad w_1 \gg w_2.$$

For illustration of numerical values in Table 9.5 are given speeds of u for atmospheric pressure and several magnitudes of T_1 and T_2. From the table it is clear that speed of wave of cooling is of the order of 1 km sec.

§ 11. Contraction of Cooling Wave Toward Center

Character of cooling and dependence of time of cooling on dimensions of heated volume in the considered case are essentially different than those which would take place during spreading of heat by the mechanism of the usual thermal conduction. During usual thermal conduction there gradually occurs similar lowering of temperature of all the mass of a body, and time of cooling of body with radius R is proportional to square of radius $t \sim R^2 c_p \rho / \varkappa$, where $\varkappa$ is coefficient of thermal conduction. During cooling by radiation along the body runs the wave, and time is proportional to first degree of radius $t \sim R/u$.

If dimensions of a heated body have the order of $R \sim 100$ m and pressure of the order of atmospheric, then during speed of wave of cooling $u \sim 1$ km/sec it contracts from the periphery to the center during the time $t \sim 0.1$ sec. During that time air is cooled from high temperatures of the order of tens and hundred thousands of degrees to temperature of transparency $T_2 \sim 10,000^\circ K$.

Lines of propagation of cooling wave together with lines of front of shock wave and boundary of fiery sphere on radius — time diagram are depicted schematically in Fig. 9.16.

Wave appears at the moment of time when temperature on the front is of the order of $2000^\circ K$.* Step will be formed in the layer with $T \sim 10,000^\circ K$, which will be approximately 10 m from the surface of the front. In the beginning, while pressure is still high ($p \sim 50$ atm at the moment of onset of step), speed of propagation of the wave along the mass is small and in spite of the fact that along the mass the wave runs deep, toward the center, in space it moves forward, being attracted by fast scattering air. Gradually the wave is delayed (in space), then turns back and "collapses" in the center.

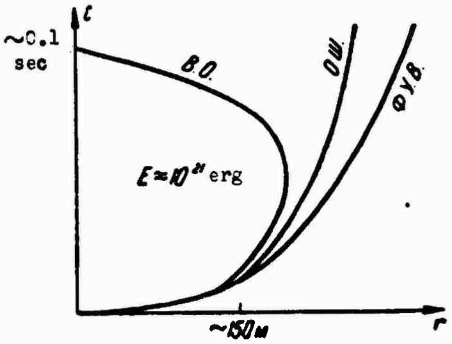

Fig. 9.16. Lines of front of shock wave (F. U. V.), boundary of fiery sphere (O. Sh.), and front of wave of cooling (V. O.) on diagram r, t. Approximate scales pertain to energy of explosion $E \approx 10^{21}$ erg.

The point of turn, determining maximum radius of surface of front of cooling wave, corresponds to zero speed of wave in space, i.e., to equality of (directed oppositely to speed of gas-dynamic scattering) particles of air and speed of propagation of wave through mass.

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*In spite of the approximate coincidence of moments of appearance of cooling wave and breakaway of front of shock wave from boundary of fiery sphere, direct physical connection between these two absolutely different phenomena is lacking.

After passage of a wave of cooling through air heated by explosion, its temperature everywhere turns out to be lower than ~$10,000^{\circ}K$, and the whole volume becomes more or less transparent. Subsequently, cooling by radiation proceeds considerably slower and has volume character, i.e., every particle emits light in accordance with its radiating ability, and this light, almost without absorption, departs from place of explosion to great distances. Certainly, volume is not completely transparent and some fraction of radiation sticks on the way in external layers, i.e., there occurs a certain transfer of energy from central regions to peripheral. In particular, this promotes nitrogen peroxide, which is contained in external layers with temperatures ~$3000-1000^{\circ}K$ (which earlier in the shock wave were heated to a temperature higher than $2000^{\circ}K$).

Similar transfer of energy occurs during passage of wave of cooling, since radiation flux, outgoing from surface of wave, partially is absorbed in "transparent" (and in reality not fully transparent) peripheral layers. In ultraviolet region of spectrum, in general, absorption is strong and ultraviolet quanta are absorbed near front of wave. This, however, does not introduce essential changes in all the above-described qualitative picture of cooling of air by the wave, founded on an assumption about high degree of transparency at temperatures lower than T_2, since in region of strong absorption with wave lengths $\lambda < 2000$ Å there is contained less than 1% of the energy of the spectrum, corresponding to a temperature of $10,000^{\circ}K$.

One should not think that after the moment of "collapse" of the wave of cooling in the center cooled air ceases to gleam and that the surface of the wave of cooling at that stage, when it still exists, also is the boundary of the fiery sphere. Air, after passing through wave of cooling, radiates fully sufficiently in order to brightly gleam even when energy effect of emission becomes small and further cooling ceases.

Wave is inside fiery sphere and collapses toward the center, leaving behind it still sufficiently strongly heated and brightly luminescent air. The boundary of the fiery sphere (i.e., boundary of glow) is composed of, at a later stage of explosion, layers with temperatures of the order of 2000-3000°K, which are cooled by radiation very slowly. After pressure becomes equal to atmospheric and motion practically ceases, these layers turn out to be practically motionless. The boundary of the fiery sphere at first moves forward from the center together with scattering air, but then is braked and remains as is shown in Fig. 9.16.

The approach of the wave of cooling to center is accompanied by a certain draining of mass of air from periphery to center, since wave leaves behind itself sharply cooled particles, and cooling during constant pressure is accompanied by compression. For instance, if in the beginning in the center temperature was 100,000°K and after "collapse" of wave became 10,000°K, where pressure at the time of collapse was not changed (remained equal to atmospheric), then air density in center is increased moreover several tens of times, which occurs because of draining of masses to center. This draining, however, does not show on far from center layers with comparatively low temperatures of the order of 2000°-3000°K, so that the position of the boundary of the fiery sphere remains constant.

On this we will end consideration of the process of cooling of air on the whole, regularities of propagation of the wave of cooling and the glow of the fiery sphere, i.e., consideration of the "macroscopic" picture.

In subsequent paragraphs we will study the internal structure of the wave of cooling; just as in gas dynamics, along with the study of general flows of gas with shock waves, it is studied by investigation of the "microscopic" picture — the internal structure of the front of a shock wave. Namely consideration of internal structure of wave of cooling permits finding the most important characteristic of a wave — radiation flux from surface of wave.

3. Structure of Front of Wave of Cooling

§ 12. Formulation of the Problem

Till now, when speaking of wave of cooling, we have considered it as some kind of a discontinuity in which temperature of gas endures a sharp jump. There was indicated the condition of energy balance, equivalent to a relationship describing the preservation of total flux of energy during flow of gas through a discontinuity, as is the case in examining shock waves. In distinction from shock waves, here it was sufficient to formulate only one energy relationship, since motion in a wave of cooling is subsonic and it is possible to disregard change of pressure during transition through front of wave (in this respect wave of cooling is similar to front of slow burning). Such "macroscopic" consideration does not permit making conclusions relative to the most important magnitude determining speed of wave, radiation flux S_2, which departs from front of wave to "infinity." For finding flux S_2 it is necessary to investigate internal structure of transition layer of front of wave, i.e., find continuous solution of equations describing transfer of radiation in wave. This was done in al. ady quoted works [16, 17].

Being distracted from concrete dimensions and form of cooled mass of gas, we will look for solution of non-stationary equations of radiant heat exchange in the form $T(x - ut)$, corresponding to plane wave, which spreads with constant speed u along gas with assigned values of temperature and density T_1, ρ_1.

Speed u should be found from equations, like determination of speed of flame in a burning mixture.

In fact equations do not have exact solution of form $T(x - ut)$. According to propagation of wave thickness is increased of layer of cooled gas, in which absorption of light although small is still different than zero, and temperature of transparency, defined by relationship $l(T_2) = d$, where under d it is possible to imply thickness of cooled layer, decreases with passage of time.

In an unlimited medium during inverse relation of mean free path on temperature the temperature of transparency, in general, turns out to be equal to zero, since layer of gas cooled to any amount of low temperatures, because of its infinite extent turns out to be absolutely opaque even during huge mean free path of radiation; radiation flux from front of wave is equal to zero and conditions of a cooling wave, in the strict sense of the word, in general, do not exist. A situation, to a certain degree analogous, takes place in the theory of stationary propagation of flame. If we do not assume that chemical reaction rate in an unburned mixture is identically equal to zero, in spite of the fact that in reality speed is final, although it is vanishingly minute, mixture will burn before it approaches flame front.

This moment, fundamental in the case of an unlimited medium creates only apparent difficulty in real conditions. After all, actually a heated, and consequently cooled by wave, region always is limited; temperature of transparency only logarithmically depends on dimensions of cooled region, i.e., weakly changes with increase of distance passed by wave, being for real bodies in very narrow limits. Additional, very slow dependence of solution on time $T(x - ut, t)$ appears only one the lowest, strongly stretched edge of the wave, in a region of already cooled, almost transparent gas. The existence of adiabatic cooling in a case when the wave spreads along expanded gas makes this additional dependence still less essential, since air, after passing through the wave, is cooled because of expansion to low temperatures and fast "skips" the temperature range in which it is still not fully transparent.

Additional, slow dependence on time $T(x - ut, t)$ will exist only in the region of purely adiabatic cooling and will hardly affect profile of temperature in the actual wave.

In order to find distribution of temperature inside front of wave of cooling, with which in turn is determined flux S_2, one should, as is usually done in the theory of conditions illustrated in Chapter VII in an example of a shock wave, consider a flat stationary process in the system of coordinates connected with the front.

In order to be free of the above-indicated difficulty and to make the problem stationary, i.e., to cross from true solution $T(x - ut, t)$ to idealized $T(x - ut)$ (in the laboratory system of coordinates), it is possible to use one of two formally artificial, but in virtue of what was said physically absolutely justified methods, responding to the real position of things.

It is possible, first, to introduce into energy equation an additional constant member A playing the role of adiabatic cooling. Magnitude A assigns constant scale d, determining temperature of transparency T_2, and limits absorption in region cooled by radiation, making optical thickness of this region final.

It is possible, secondly, not to consider adiabatic cooling, but then from the very beginning to introduce temperature of transparency T_2 on the basis of appraisal of type (9.9), and to assume formally that at $T < T_2$ the medium absolutely is transparent (mean free path $l = \infty$). Then gas will be cooled only to temperature T_2, after which emission, proportional to $\varkappa = 1/l$, and further cooling will cease.

Inasmuch as motion of gas in wave of cooling is subsonic (appraisals have attested to this), kinetic energy of gas flow it is possible to disregard as compared to thermal. Equation of energy at current point x inside the wave is recorded in general taking into account additional member describing adiabatic cooling in the form

$$u\rho_1 c_p \frac{dT}{dx} + \frac{dS}{dx} = -A, \quad A > 0. \qquad (9.10)$$

If one were to not assume heat capacity constant, this equation is conveniently recorded through specific enthalpy of gas:

$$u\rho_1 \frac{dw}{dx} + \frac{dS}{dx} = -A. \qquad (9.11)$$

Here S is energy flow of radiation at point x of wave (in virtue of preservation of flux of mass $\rho u(x) = \rho_1 u$, where u is speed of wave, equal to speed of gas influx into wave, ρ_1 is initial density of gas, and ρ and $u(x)$ are magnitudes at current point x.

Directions of flow, of axis x, and of speed are shown in Fig. 9.15, where schematically is depicted temperature gradient in front of wave. Gas flows into wave from the left to the right; wave spreads along undisturbed gas from the right to the left. Before wave, at $x = -\infty$, temperature has the given value $T = T_1$, and flow $S = 0$, in accordance with remark made in § 10 about the fact that radiant thermal conduction in highly heated gas is immaterial and flow in this region is small. Radiation flux S changes during growth of x from $-\infty$ to $+\infty$ from zero to magnitude S_2, equal to flux departing from front of wave to "infinity."

If one were to not consider adiabatic cooling, but to assume temperature of transparency T_2 assigned (second method), then equation of energy (9.11) gives integral

$$S = u\rho_1 (w_1 - w). \tag{9.12}$$

Here constant of integration is expressed through enthalpy of initial gas $w_1 = w (T_1)$, in accordance with boundary condition $x = -\infty$, $T = T_1$, $S = 0$. Being applied to lower part of wave, where $T = T_2$ and flux is equal to flux departing to infinity $S = S_2$, integral of energy (9.12) leads, as one should have expected, to equation of energy balance (9.6), connecting value of magnitudes on both sides of front of wave, if the latter is considered as a discontinuity.

To equation of energy it is necessary to join equation of transfer of radiation with which is determined flux S. Let us, as when examining structure of front of shock wave taking into account radiation (see Chapter VII, § 3), describe transfer of radiation in diffusion approximation.

Furthermore, we will introduce, as earlier, a certain mean free path, averaged over the spectrum, of quanta l. Equations of diffusion approximation are written then in the form

$$\frac{dS}{dx} = c\,\frac{U_p - U}{l}, \tag{9.13}$$

$$S = -\frac{lc}{3}\,\frac{dU}{dx}, \tag{9.14}$$

where U is true density of radiation, and U_p is equilibrium density, corresponding to temperature of substance at point x: $U_p = \frac{4\sigma T^4}{c}$.

As will be shown below, density of radiation in a considerable part of the wave is close to equilibrium. In these conditions, as it is known (see § 12, Chapter II), spectral mean free path l_ν is averaged according to Rosseland. In the region of strongly cooled air there is no local equilibrium and the Rosseland method of averaging does not fit. The method of averaging, however, cannot introduce qualitative changes in the results of consideration, since exponential Boltzmann factor of type $e^{I/kT}$, effectively describing basic temperature dependence of mean free path, is kept during any averaging, and on the pre-exponential factor, which, of course, changes during change of method of averaging, all effects in the wave depend very weakly, logarithmically, as temperature of transparency T_2. Therefore, for simplicity, we will imply always under $l(T)$ Rosseland mean free path.

In equations (9.13), (9.14) it is convenient to cross to optical coordinate τ, which we will count off from point $x = +\infty$, where gas is transparent and $l = \infty$ (axis τ is directed oppositely to axis x):

$$d\tau = -\frac{dx}{l}, \quad \tau = -\int_{+\infty}^{x} \frac{dx}{l} = \int_{x}^{+\infty} \frac{dx}{l}.$$

Equations (9.13) and (9.14) take the form

$$\frac{dS}{d\tau} = -c(U_p - U), \tag{9.15}$$

$$S = \frac{c}{3}\frac{dU}{d\tau}. \tag{9.16}$$

To equations of transfer of radiation it is necessary to join boundary conditions. On the upper edge of the wave during $\tau = \infty$, as already was mentioned above,

$$\tau = \infty, \quad S = 0, \quad T = T_1. \tag{9.17}$$

On the lower edge of the wave, which is the boundary between absorbing and absolutely transparent media (vacuum), one should subordinate flux and density of radiation to known diffusion condition on the boundary of a medium with vacuum (see formula (2.66)):

$$\tau = 0, \quad S_1 = \frac{cU_1}{2}. \tag{9.18}$$

Equation of transfer of radiation together with equation of energy and boundary conditions completely determine structure of front of wave, flux S_2, and speed u.

§ 13. Radiation Flux from Surface of Front of Wave

Practical interest is presented mainly by strong waves of cooling, in which gas being cooled from initial temperature T_1 to temperature of transparency T_2 de-excites a considerable fraction of its own energy: $T_1 \gg T_2$. Weak waves, where the difference between T_1 and T_2 is small,* are interesting basically from the methodical point of view, inasmuch as in this case it is possible to obtain exact analytical solution of equations. It is clear that in weak wave radiation flux from front S_2, included in interval $\sigma T_1^4 > S_2 > \sigma T_2^4$, is determined quite exactly in virtue of proximity of extreme values; therefore, question about flux, which is the main one, actually does not appear: $S_2 \approx \sigma T_2^4 \approx \sigma T_1^4$. Analytic solution for a weak wave can be found in work [16]: here we will not pause on it and will cross directly to the consideration of a strong wave of cooling.

In the preceding paragraph it was shown that for finding steady-state operation it is necessary to use one of the two methods: either to introduce into energy equation a constant member of adiabatic cooling, or, from the very beginning, to determine temperature of

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*With this, however, in spite of proximity of T_1 and T_2, it is assumed that temperature dependence of mean free path $l(T)$ is so sharp that $l(T_1) \ll l(T_2)$. The latter is a condition of the actual existence of a wave of cooling.

transparency T_2, and to consider that at $T < T_2$ gas is absolutely transparent ($l = \infty$), thereby excluding from consideration region already cooled by radiation, which absorbs light very weakly. The first method gives a more complete picture of distribution of temperature, since it permits investigating movement of temperature in cooled air and to consider weak absorption in it. However, it leads to unnecessary mathematical complications in examining profile of temperature inside the actual wave (at temperatures higher than temperature of transparency) and in determining flow departing from front of wave to infinity. Meanwhile inside the wave adiabatic cooling is small compared to cooling because of radiation; therefore, it is more preferable to investigate the internal structure of the wave, using the second method. In § 15 there will be noted certain peculiarities of conditions, connected with the existence of adiabatic cooling.

In the absence of adiabatic cooling the integral of energy equation is given by formula (9.12), which we will copy, while considering, for simplicity, heat capacity to be constant:

$$S = u\rho_1 c_p (T_1 - T). \qquad (9.19)$$

The problem consists of the solution of system of equations (9.15), (9.16), (9.19) together with boundary conditions (9.17), (9.18).

Before we investigate this system, we will try to estimate radiation flux S_2, departing from front, based on the most general physical considerations. This consideration will tell us the approximation which can be made during solution of the system of equations and finding the profile of temperature in the wave.

Owing to the actual formulation of the problem, the temperature at no point of the wave can be lower than temperature of transparency

T_2, since gas, after being cooled to temperature T_2, ceases to absorb and to emit radiation, and further cooling is ceased. Consequently, T_2 is minimum temperature in the wave and near the lower edge of the wave temperature grows according to distance from boundary with "vacuum" — with absolutely transparent region, where $T = T_2$ and $l = \infty$. Thus, on the lower edge at $\tau = 0$ $\frac{dT}{d\tau} \geq 0$. From energy equation (9.19) it follows that flux, during removal from lower edge to depth of wave, decreases, i.e., at $\tau = 0$ $dS/d\tau \leq 0$. Equation of "continuity" of radiation (9.15) indicates that with this, density of radiation on the lower edge of the wave is not higher than equilibrium density $U_2 \leq U_{p2} = \frac{4\sigma T_2^4}{c}$ (divergence of flux dS/dx is not negative; matter is not heated by radiation). In diffusion approximation is flow boundary of medium with vacuum is connected with radiation density by condition (9.18): $S_2 = cU_2/2$. Noticing that $U_2 \leq U_{p2}$, we will find that flux S_2 is limited from above by magnitude $2\sigma T_2^4$. Actually,

$$S_2 = \frac{cU_2}{2} < \frac{cU_{p2}}{2} = 2\sigma T_2^4.$$

On the other hand, effective temperature of radiation T_{ef}, determined by equality $S_2 = \sigma T_{ef}^4$, coincides with a certain average temperature of radiating layer and, consequently, cannot be lower than T_2 since temperature of substance in radiating layer, as also at any other point of wave, is always higher than T_2. It follows from this that $S_2 > \sigma T_2^4$, and flux S_2, departing from front of wave to infinity, turns out to be included in very narrow limits:

$$\sigma T_2^4 < S_2 < 2\sigma T_2^4, \tag{9.20}$$

$$T_2 < T_{ef} < \sqrt[4]{2}T_2. \tag{9.21}$$

Thus, independently of amplitude of wave, at any amount of high initial temperatures T_1 the lowest edge of wave always radiates, and radiation flux from surface of front of wave corresponds to temperature close to T_2. In no case should one think that here some role is played by the (accepted by us for description of transfer of radiation) diffusion approximation leading to boundary condition (9.18). Really, diffusion condition (9.18) corresponds to the assumption that quanta going out from a medium in a vacuum, are distributed on isotropic angles, and from the vacuum into the medium quantum do not proceed (in the vacuum there are no sources of light).

Even if we took another border assumption about the fact that there is sharply expressed anisotropy of radiation on a boundary with a vacuum and all quanta emerge from the medium normally to its surface, diffusion condition (9.18) would be changed by condition $S_2 = cU_2$, which would lead to inequalities $\sigma T_2^4 < S_2 < 4\sigma T_2^4$, $T_2 < T_{ef} < \sqrt[4]{4}T_2$, differing from (9.20), (9.21) by an immaterial numerical factor.

In reality limitation of flux $S_2 < 2\sigma T_2^4$ is connected with stationariness of conditions of cooling, because of which profile of temperature, completely determining flux, cannot be arbitrary and is established fully by determination in accordance with equations of conditions.

From inequality (9.21) there ensues an important corollary, which permits solving the entire problem about structure of front, described by nonlinear equations, by the simplest method. Radiation of a heated body adjoining a transparent medium (or vacuum) is generated basically in the layer near the surface of a body having optical thickness of the order of unity or several units (quanta generated in deeper layers are not in a state to emerge outside, almost completely being absorbed along the path). Effective temperature of radiation coincides with a certain average temperature of this radiating layer. But because of inequality (9.21) effective temperature is very close to temperature of lower edge of wave T_2. This means, temperature of matter after point $\tau = 0$, where $T = T_2$, changes very little at an optical distance of the order of several units in depth of wave. This permits making the following conclusion.

In a strong wave of cooling in which $T_1 \gg T_2$, radiation flux on lower edge of wave, in radiating layer, changes little and is almost constant. Really, during change of temperature $\Delta T \lesssim T_2$ flux changes to magnitude

$$|\Delta S| \sim u\rho_1 c_p \Delta T \lesssim u\rho_1 c_p T_2,$$

and at $T_1 \gg T_2$ flux at point $\tau = 0$, $T = T_2$ is equal approximately to $S_2 \approx u\rho_1 c_p T_1$ (see (9.19)). Consequently,

$$\frac{|\Delta S|}{S_2} \approx \frac{T_2}{T_1} \ll 1.$$

Inasmuch as flux on lower edge of a strong wave is almost constant, situation is fully analogous to position in photospheres of stationary stars, where radiation flux is strictly constant. Thus, problem determining connection of flux S_2 with temperature of transparency T_2 (temperature on boundary of a medium with a vacuum) in the limit of a strong wave is equivalent to known problem of Milne (see § 15, Chapter II). It has exact solution during strict calculation of angular distribution of radiation

$$S_2 = \frac{4}{\sqrt{3}} \sigma T_2^4, \tag{9.22}$$

only somewhat differing from solution in diffusion approximation:

$$S_2 = 2\sigma T_2^4. \tag{9.23}$$

Hence, one should mention, it is clear that in the framework of the diffusion approximation flow value S_2 in the limit of a strong wave coincides with upper boundary of inequality (9.20).

§ 14. Distribution of Temperature in the Front of a Strong Wave

The fact that temperature only slightly changes during the extent of a radiating layer with optical thickness of the order of several units testifies to the existence of local equilibrium of radiation with matter. Relative deviation of density of radiation on lower edge of wave from equilibrium is less the stronger the wave, i.e., the larger the ratio T_1/T_2. Actually, from equation (9.15) it follows that

$$\left(\frac{U_p - U}{U_p}\right)_{\tau=0} = \frac{U_{p2} - U_2}{U_{p2}} = -\frac{1}{cU_{p2}}\left(\frac{dS}{d\tau}\right)_2.$$

But because of the above said

$$\left|\frac{dS}{d\tau}\right|_2 \sim \frac{|\Delta S|}{\Delta\tau} \leqslant S_2\frac{T_2}{T_1} = 2\sigma T_2^4\frac{T_2}{T_1},$$

since $|\Delta S| \sim S_2\, T_2/T_1$ is change of flux during the period of optical distance $\Delta\tau \sim 1$. Consequently, relative deviation of density of radiation from equilibrium in strong wave is

$$\frac{U_{p2} - U_2}{U_{p2}} \sim \frac{S_2}{cU_{p2}}\frac{T_2}{T_1} \sim \frac{T_2}{T_1} \ll 1.$$

It is possible to show that during removal in depth of wave from its lower edge, relative deviation, i.e., degree of nonequilibrium of radiation, only decreases, so that if wave is sufficiently strong and deviation on lower edge is small, then condition of local equilibrium is executed on the entire extent of the wave.* Thus, equations

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*This proves, by the way, that in the case of a strong wave, as mean free path of radiation it is possible to use Rosseland average.

describing structure of the front of a strong wave of cooling are possible to solve in an approximation of radiant thermal conduction, considering

$$S \approx \frac{c}{3}\frac{dU_p}{d\tau} = \frac{16\sigma T^3}{3}\frac{dT}{d\tau}.$$

Combining this equation with expression (9.19), we will obtain equation for function $T(\tau)$, which is integrated in quadratures.

On lower edge of wave we obtain approximate form of solution, which, naturally, coincides with diffusion solution of problem of Milne, since flux $S \approx$ const (see § 15, Chapter II):

$$T = T_2\left(1 + \frac{3}{2}\tau\right)^{\frac{1}{4}}. \tag{9.24}$$

Asymptotic profile of temperature on upper edge of a strong wave has the form

$$T = T_1\left(1 - e^{-\frac{\tau}{\tau_k}}\right), \quad \tau \gg \tau_k, \tag{9.25}$$

where magnitude τ_k, which can be considered as effective optical thickness of wave, depends only on amplitude of wave:

$$\tau_k \approx \frac{8}{3}\left(\frac{T_1}{T_2}\right)^4.$$

Optical thickness of wave sharply increases with increase in ratio T_1/T_2. We will not introduce here general expression for profile $T(\tau)$, which on lower and upper edges is simplified, obtaining the form (9.24), (9.25) (see [17]), but we will depict profile of temperature on graph. Fig. 9.17 pertains to case $T_1/T_2 = 5$, $\tau_k = 1670$.

Knowing profile $T(\tau)$ and mean free path depending upon temperature, it is easy to find distribution of temperature with respect to geometric coordinate with the help of determination $-x = \int_0^\tau l\,(T)\,d\tau$.*

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*Inasmuch as in fact $l(T_2) \neq \infty$, temperature on lower edge aspires to magnitude T_2 not asymptotically, but with slope different than zero. Therefore, origin of coordinates $x = 0$ it is possible to place at point where $\tau = 0$, $T = T_2$.

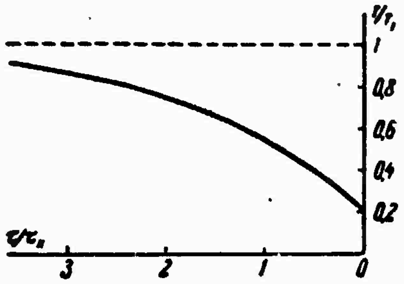

Fig. 9.17. Distribution of temperature with respect to optical coordinate in wave of cooling with $T_2/T_1 = 5$; $\tau_k = 1670$.

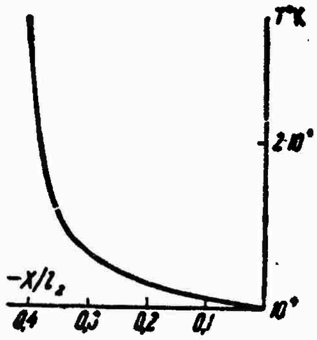

Fig. 9.18. Distribution of temperature with respect to geometric coordinate on lower edge of wave of cooling; $T_2 = 10{,}000^\circ K$.

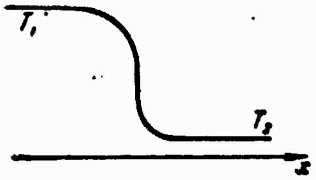

Fig. 9.19. Profile of temperature in wave of cooling.

In Fig. 9.18 is presented distribution temperature $T(x)$ on lower edge of wave for case of Boltzmann dependence $l(T) = \text{const} \exp(I/kT)$. As scale of length is accepted magnitude $l_2 = l(T_2)$; temperature of transparency is taken as equal to $T_2 = 10{,}000^\circ K$. Fig. 9.18 shows that wave has the form of a step. In fact, Boltzmann dependence $l(T)$, ensuring sharp step of temperature in wave, takes place only below temperature ~30,000-40,000°K, until multiple ionization of gas starts. At higher temperatures mean free path passes through minimum and starts to grow with temperature increase. Therefore, upper edge of sufficiently strong wave with $T_1 \sim 50{,}000$-$100{,}000^\circ K$ is strongly stretched (at $l = \text{const}$ profile $T(x)$ on upper edge would coincide with profile $T(\tau)$) by the formula (9.25). Approximate distribution of temperature in wave with $T_1 = 40{,}000^\circ K$ is shown in Fig. 9.19.

If one were to be distracted from the lengthiness of the upper edge of the wave, which unessentially shows on cooling conditions of air (since flux and divergence of flux, determining cooling on upper edge, are very small), then geometric width of the step will compose, as one may see from Fig. 9.18, several tenths of mean free path $l(T_2)$. At $T_2 \sim 10{,}000^\circ K$ and $l_2 \sim 10$ m width of wave turns out to be of the order of several meters, i.e., wave of cooling, spreading through a large volume of air with a radius of a hundred meters, is indeed narrow and can be considered as a discontinuity of temperature and density of substance (but not pressure, which changes only slightly during the period of the wave).

§ 15. Calculation of Adiabatic Cooling

In preceding paragraphs by means of artificial cutting of absorption at a temperature of transparency T_2 ($l = \infty$ at $T < T_2$) there was excluded from consideration the region of cooled air with temperatures lower than the temperature of transparency. In reality in this region absorption although small is still certain, therefore, it is natural to inquire how temperature behaves in the zone of cooled gas, which occurs with radiation flux outgoing from front of wave. Process in this region is essentially nonstationary; it depends on concrete conditions: dimensions, hydrodynamic motion, mechanisms of absorption of light. We will consider here that practically important case, when wave of cooling spreads not along motionless, and along expanded air, and air cooled by radiation continues to be cooled adiabatically. Adiabatic cooling quickly brings air to a temperature zone of total transmittance, which does not render influence on conditions of cooling wave. During a period of comparatively small time, while adiabatically cooled air still to some amount noticeably absorbs light, speed of adiabatic cooling changes only slightly.

Therefore, process with adiabatic cooling it is possible approximately to consider stationary and to describe it by energy equation (9:10) with constant member A. Integral of this equation is:

$$u\rho_1 c_p T + S = -Ax + \text{const.} \tag{9.26}$$

Constant of integration here is arbitrary, since it is determined simply by selection of the beginning of reading of coordinate x; it is possible to assume that it is equal to zero.

On the upper edge of wave at $x \to -\infty$ flux $S \to 0$. It can appear that this artificially imposed condition contradicts the fact of the existence of a gradient of temperature, connected with presence of adiabatic cooling. However, it is assumed that mean free path $l(T)$ so fast decreases with temperature rise that product $S \sim -l(T)\,T^3\,\frac{dT}{dx}$ aspires to zero at $T \to \infty$, which is physically justified, since flux of radiant thermal conduction from within, from the zone of burning air is very small. On the lower edge of the wave at $x \to +\infty$ flux aspires to constant S_0—flux departing to infinity.* Therefore temperature in wave at $x \to \pm\infty$ asymptotically aspires to two straight lines:

$$u\rho_1 c_p T = -Ax \text{ at } x \to -\infty,$$

$$u\rho_1 c_p T = -Ax - S_0 \text{ at } x \to +\infty.$$

These straight lines are shifted along an ordinate to magnitude S_0 (in Fig. 9.20 they are shifted to segment $S_0/u\rho_1 c_p$). The problem consists in determining this magnitude S_0. We will not expound here the mathematical solution (see [17]); we will be limited by qualitative consideration of the course of the process.

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*This flux, as we will see below, is somewhat different than flux S_2 departing from effectively defined surface of front of wave.

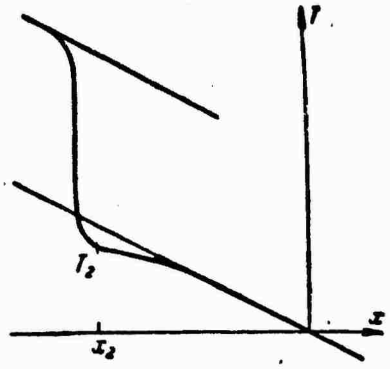

Fig. 9.20. Profile of temperature in a wave of cooling during the calculation of adiabatic cooling.

Let us trace the consecutive change of the state of a particle of gas, entering into the wave of cooling, i.e., we will advance from $-\infty$ in a positive direction to axis x (Fig. 9.20). At first, at very high temperatures, radiant thermal conduction is insignificant, and the particle is cooled purely adiabatically; the temperature of it drops along the upper straight line. Then the particle starts even more and more to be cooled by radiation and the temperature of it descends below the upper straight line. Density of radiation in the particle with this is less than equilibrium (the particle emits more light than it absorbs), and the radiation flux in it grows.

In this stage speed of radiant cooling is considerably larger than speed of adiabatic, and temperature steeply drops (particle passes through wave of cooling). Thus it continues until particle is cooled to so low a temperature that speed of radiant heat exchange becomes less than speed of adiabatic cooling.

Due to an extraordinarily sharp fall of absorption (and emission) with lowering of temperature, the already small adiabatic cooling after that moment makes the particle quite transparent, and radiant heat exchange ceases altogether.

Density of radiation, which is determined by flux being generated in more heated layers and passing through particles, remains almost constant. Equilibrium density of radiation, proportional to T^4, fast decreases. Therefore, in "transparent" region, in distinction from "opaque", density of radiation is higher than equilibrium, absorption exceeds emission, and the particle is heated by radiation; radiation flux is weakened, as is shown in Fig. 9.21.*

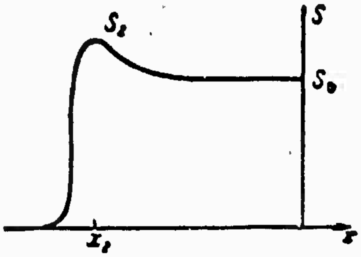

Fig. 9.21. Flux distribution of radiation in wave of cooling during calculation of adiabatic cooling.

Consequently, on axis x there exists such a point $x = x_2$ (corresponding to it, temperature and flux we will designate by T_2, S_2), which divides region of "opaque" air, intensely cooled by radiation, and almost transparent air, weakly heated by radiation. At this point density of radiation is accurately equal to equilibrium $U_2 = U_{p2}$; divergence of flux is equal to zero and flux is maximum $S_{max} = S_2$.

Naturally this point, at which cooling of air by radiation is ceased, is considered the lower boundary of the wave of cooling; temperature in it is T_2 – temperature of transparency – and flow S_2 is flow going out from the surface of the front of the wave. Absorption of this flow in "transparent" zone is small, so that to infinity departs flow S_0, only somewhat smaller than S_2.

Profiles of temperature and flow T(x), S(x), answering the described picture, are depicted in Figs. 9.20, 9.21. At low temperatures curve T(x) is spread below lower asymptotic straight line, nearing it from below, since gas is heated by radiation: maximum of flow lies at the point where temperature strongest of all deviates from a straight line downward (this follows from equation (9.26)).

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*This situation somewhat reminds us of the position in the front of a shock wave radiation: after shock discontinuity density of radiation is less than equilibrium; gas is cooled by radiation and sends flow into region before discontinuity, where flow is absorbed, density of radiation is higher than equilibrium, and gas is heated.

It is possible to show that flux S_2 is connected with temperature of transparency by the same relationship as in a wave without adiabatic cooling $S_2 = 2\sigma T_2^4$. Regarding the actual temperature of transparency, it is possible to estimate it from the condition that at a temperature close to T_2 speed of radiant cooling is comparable with speed of adiabatic cooling A by which approximately is determined lower edge of wave.

Temperature T_2 depends on arbitrarily assigned magnitude A only logarithmically in virtue of exponential dependence $l(T)$, just as earlier it logarithmically depended on arbitrarily assigned characteristic scale of length d (according to condition $l(T_2) = d$). In this case the characteristic scale is the distance at which temperature drops due to adiabatic cooling from magnitude T_2 to zero, which, incidentally, also determines position of lower edge of wave, i.e., coordinate x_2. Actually for determination of temperature of transparency there remains condition $l(T_2) \approx d$, only now there is assigned no actual magnitude d, and magnitude A, with which scale d is connected.

Literature

1. I. Sh. Model'. ZhETF, 32, 714 (1957).

2. Ya. B. Zel'dovich. ZhETF, 32, 1126 (1957); Ya. B. Zel'dovich and Yu. P. Rayzer. UFN, 63, 613 (1957).

3. Yu. P. Rayzer. ZhETF, 32, 1528 (1957).

4. Yu. P. Rayzer. ZhETF, 33, 101 (1957).

5. M. P. Vanyukov and A. A. Mak. UFN, 66, 301 (1958).

6. E. G. Schneider. J. Opt. Soc. Amer., 30, 128 (1940).

7. K. K. Aglintsev. Dosimetry of ionizing radiations, State Technical Press, p. 46, 1950.

8. Landholt. Tables 1, Part I, 6th edition, 1950, p. 316.

9. R. H. Messner. Z. f. Phys., 85, 727 (1933).

10. E. Dershem. Phys. Rev., 37, 1238 (1931).

11. The Effects of Atomic Weapons. New York — Toronto — London, 1950.

12. The Effects of Nuclear Weapons, Military Publishing House, 1960.

13. L. I. Sedov. Methods of similarity and dimension in mechanics, 4th edition, State Technical Press, 1957.

14. Yu. P. Rayzer. Journal of physical Chemistry, 33, 700 (1959).

15. Yu. P. Rayzer. ZhETF, 34, 483 (1958).

16. Ya. B. Zel'dovich, A. S. Kompaneyets, and Yu. P. Rayzer. ZhETF, 34, 1278 (1958).

17. Ya. B. Zel'dovich, A. S. Kompaneyets, and Yu. P. Rayzer. ZhETF, 34, 1447 (1958).

CHAPTER X

THERMAL WAVES

§ 1. Thermal Conduction of a Substance

If a body is heated nonuniformly or in it there occurs energy release, there appears a heat flux transferable by means of thermal conduction. Thermal conduction promotes propagation of energy and thermal balance. Along with gradients of temperature, in general, there also appear gradients of pressure, owing to which the substance is set into motion. In many cases hydrodynamic transfer of energy predominates over thermal conduction. However, frequently the motion and hydrodynamic transfer of energy are immaterial and heat from sources spreads only by means of thermal conduction. At low temperatures the mechanism of heat transfer is the ordinary thermal conduction of the substance.

In the ordinary thermal conduction, thermal perturbations are propagated in the medium comparatively slowly (subsequently this will be shown in the example of a gas). Small perturbations of pressure spread with transonic speed at the expense of a certain redistribution of density, and pressure is balanced much faster than temperature. If changes of temperature in the medium are small, the speed of the substance is much less than the speed of sound and in the study of propagation of heat by means of thermal conduction the motion of the substance can frequently be disregarded, considering that the process occurs at constant pressure.

Equation of energy balance then has the form

$$\rho c_p \frac{\partial T}{\partial t} = -\operatorname{div} S + W, \tag{10.1}$$

where ρ is the density which can approximately be considered as constant, c_p is the specific heat capacity at constant pressure, S is the vector of heat flux, and W is the energy release in 1 cm^3 per sec from outside sources.

Thermal conduction of heat flux in first approximation is proportional to the gradient of temperature:

$$S = -\varkappa \operatorname{grad} T, \tag{10.2}$$

where $\varkappa$ is the coefficient of thermal conduction, depending on the properties of the substance. Putting expression (10.2) in the equation of energy balance (10.1), we obtain a general heat-conduction equation which describes the temperature of the medium depending upon coordinates and time:

$$\rho c_p \frac{\partial T}{\partial t} = \operatorname{div}(\varkappa \operatorname{grad} T) + W. \tag{10.3}$$

In a not too large range of temperatures the coefficient of thermal conduction and heat capacity of the substance hardly change and are practically constant. Heat-conduction equation (10.3) is then linear (with the exception of cases when energy release W depends on temperature in nonlinear form).

When $\varkappa$ = const, we have

$$\rho c_p \frac{\partial T}{\partial t} = \varkappa \Delta T + W. \tag{10.4}$$

If one were to divide the heat-conduction equation (10.4) by ρc_p, it takes on the form in which the properties of the substance are characterized by only one parameter: the coefficient of heat transfer $\chi = \varkappa/\rho c_p$:

$$\frac{\partial T}{\partial t} = \chi \Delta T + q, \quad q = \frac{W}{\rho c_p}. \tag{10.5}$$

In gases the coefficient of heat transfer is approximately equal to the coefficient of diffusion of molecules:

$$\chi = \frac{l_a \bar{v}}{3},$$

where l_a is the range of molecules, and $\bar{v}$ is their average thermal speed; for instance, in air under normal conditions $\chi = 0.205$ cm^2/sec. In liquids and solids the mechanisms of thermal conduction are more complicated. We will not remain on this question here. Let us indicate that in water at room temperature $\chi = 1.5 \cdot 10^{-3}$ cm^2/sec.

To the heat-conduction equation one should add initial and boundary conditions. At the initial moment there sets-in distribution of temperature in the medium:

$$T(x, y, z, 0) = T_0(x, y, z). \tag{10.6}$$

On the boundaries of two media 1 and 2 with different properties the heat flux is continuous

$$(\varkappa \operatorname{grad} T)_1 = (\varkappa \operatorname{grad} T)_2. \tag{10.7}$$

On the boundaries of the considered body there are given, as functions of time, the temperature or flux of heat or, in general, the bond between them.

Mathematical theory of linear thermal conduction, which is concerned with the solution of equation (10.5) in reference to different specific problems, is well developed and is widely applied in the most diverse regions of physics and technology.

§ 2. Nonlinear (Radiant) Thermal Conduction

At high temperatures of the order of tens and hundreds of thousands of degrees there appears a completely different mechanism of heat transfer, i.e., radiant thermal conduction. We became acquainted in detail with the process of radiant thermal conduction in Chapter II, and also in Chapters VII and IX, where we considered problems about the structure of the front of a very intense shock wave and about cooling of air by radiation.

An essential distinction of radiant thermal conduction from the ordinary consists in that the coefficient of radiant thermal conduction strongly depends on temperature, owing to which the heat-conduction equation is nonlinear.

The heat flux transferable by the mechanism of radiant thermal conduction is equal to (see formula (2.76)):

$$S = -\frac{lc}{3}\operatorname{grad} U_p = -\frac{lc}{3}\operatorname{grad}\frac{4\sigma T^4}{c}, \tag{10.8}$$

where $U_p = 4\sigma T^4/c$ is the density of energy of equilibrium radiation, and l is the Rosseland path of light.* Energy flow (10.8) can be recorded through the gradient of temperature in the form of (10.2), if one determines the coefficient of radiant thermal conduction by the formula

$$\varkappa = \frac{lc}{3}\frac{dU_p}{dT} = \frac{16\sigma T^3 l}{3}. \tag{10.9}$$

Coefficient of radiant thermal conduction depends on temperature both due to the proportionality of heat capacity of radiation $c_{rad} = dU_p/dT \sim T^3$, and also due to the dependence on temperature of the radiation path l.

In the radiant mechanism of thermal conduction the energy can spread with a speed much larger than the speed of sound in the substance. This is connected with the fact that the speed of light at non-relativistic temperatures is many times greater than the speed of sound. If in a body there takes place energy release and the substance is heated to a sufficiently high temperature, this energy in the

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*Let us recall that transfer of radiation has the character of thermal conduction if the density of energy of radiation in every point of the medium is close to equilibrium. For this it is necessary, that the dimensions of the heated region considerably exceed the range of radiation.

beginning spreads quickly by means of radiant thermal conduction. Although the speed of propagation of heat is much larger than the speed of sound, the substance does not succeed to come into motion, the pressure in it does not succeed in being balanced, and the heat spreads through the motionless substance. Subsequently there will be given an appraisal of the conditions at which there appears motion. We will consider here the propagation of heat by means of radiant thermal conduction only in a motionless medium, the density of which does not change with the passage of time.

Energy balance, as before, is described by equation (10.1) or (10.3) (but not (10.4), since $\varkappa \neq \text{const}$), with the only difference that instead of heat capacity at constant pressure c_p, in the equation one should put heat capacity at constant volume c_V. It is then assumed that the density of energy of radiation U_p can be disregarded as compared to the density of energy of the substance $\rho\varepsilon(T)$.

If one approximately considers heat capacity c_V as a magnitude, not depending on temperature, and divides the heat-conduction equation by ρc_V, we obtain the equation

$$\frac{\partial T}{\partial t} = \operatorname{div}(\chi \operatorname{grad} T) + q, \tag{10.10}$$

corresponding to equation (10.5). Coefficient of radiant thermal transfer χ is equal to

$$\chi = \frac{\varkappa}{\rho c_V} = \frac{lc}{3}\frac{c_{\text{изл}}}{\rho c_V}. \tag{10.11}$$

There is a deep parallel between this magnitude and the coefficient of ordinary thermal conduction of a gas $\chi = l_a\bar{v}/3$. This coincides with the coefficient of diffusion of molecules which are heat carriers. In radiant thermal conduction the substance is heated and cooled, and the energy carrier is the radiation, which plays the role of an "intermediary." Therefore, the coefficient of radiant heat transfer is not simply equal to the coefficient of diffusion of radiation $lc/3$, but is still proportional to the ratio of heat capacities of radiation and the substance.

In many cases the range of light l can be approximately considered as an exponential function of temperature (density of the medium is considered to be constant):

$$l = AT^m, \quad m > 0. \tag{10.12}$$

In a completely ionized gas, where the mechanism of radiation and absorption of light is purely a braking mechanism, m = 7/2. In the region of multiple ionization of gases m ~ 1.5–2.5.

At exponential law (10.12) the coefficient of radiant heat transfer is also on exponential function:

$$\varkappa = \frac{16\sigma A}{3} T^n = BT^n, \quad n = m + 3, \tag{10.13}$$

where index n ~ 4.5–5.5 in the region of multiple ionization. In the approximation in which the heat capacity of a gas is considered to be constant, we arrive at equation (10.10) with coefficient of radiant heat transfer, equal to

$$\chi = \frac{\varkappa}{\varrho c_V} = \frac{B}{\varrho c_V} T^n = aT^n. \tag{10.14}$$

Equation of nonlinear thermal conduction has the form

$$\frac{\partial T}{\partial t} = a \operatorname{div}(T^n \operatorname{grad} T) + q. \tag{10.15}$$

Usually at high temperatures in the region of multiple ionization the specific heat capacity and internal energy of a gas can be approximated by exponential functions of temperature:

$$\varepsilon = \alpha T^{k+1}, \quad c_V = \frac{\partial \varepsilon}{\partial T} = (k+1)\alpha T^k,$$

where α is a constant, and k is a magnitude equal approximately to 0.5 (see § 8, Chapter III). In the root law of heat capacity the heat-conduction equation can also be reduced to the form of (10.15). Let us introduce, instead of temperature, as an unknown function, the internal energy of a unit of volume

$$E = \varrho a T^{k+1}, \quad T = \left(\frac{E}{\varrho a}\right)^{\frac{1}{k+1}}.$$

We obtain

$$\frac{\partial E}{\partial t} = a' \operatorname{div}(E^{n'} \operatorname{grad} E) + q', \tag{10.16}$$

where

$$n' = \frac{n-k}{k+1}, \quad a' = \frac{B}{(k+1)(\varrho a)^{\frac{n+1}{k+1}}}, \quad q' = W. \tag{10.17}$$

Equation (10.16) does not differ from equation (10.15); their solutions also coincide. In order to cross from the solution of equation (10.15) $T = T(x, y, z, t)$ for any specific problem, to the solution of equation (10.16) $E = E(x, y, z, t)$ for the same problem, one should only replace constants a and n by a' and n, and also replace the function of the source q by $q' = W = q\rho c_V$. Let us note that when $n = 5$, $k = 0.5$, and $n' = 3$.

Subsequently for convenience of comparing the conclusions of theories of nonlinear and linear thermal conduction, we will originate from equation (10.15) for temperature. We will then consider that the found solution of any specific problem can be immediately recorded for the case of exponential dependence of heat capacity on temperature.

Besides radiant thermal conduction, which presents the biggest interest, there exists one more example of nonlinear thermal conduction. This is electron thermal conduction in plasma, which we were concerned with in § 12 of Chapter VII. (Ionic thermal conduction of plasma also strongly depends on temperature, but it plays a considerably smaller role than electron thermal conduction.) Coefficient of electron heat transfer is $\chi_e \sim T_e^{5/2}$.

It is interesting that a nonlinear heat-conduction equation of the type (10.15) describes a completely different process, namely the motion of a polytropic gas (pressure and density of which are connected by the equation $p = \text{const}\ \rho^n$) in a porous medium. Density of gas ρ satisfies the equation:

$$\frac{\partial \varrho}{\partial t} = b\,\mathrm{div}\,(\varrho^n\,\mathrm{grad}\,\varrho),$$

where n is the polytropic exponent, and b is a constant which is determined by the porosity and permeability of the medium and properties of the filtering gas.

Specific problems of nonlinear thermal conduction correspond to the same problems of the theory of filtration.

Processes of nonlinear thermal conduction for the first time were considered by Ya. B. Zel'dovich and A. S. Kompaneyets [1], who, in particular, found the exact solution of the problem about propagation of heat from an instantaneous plane source. Corresponding questions of the theory of filtration were independently investigated by G. I. Barenblatt [2]. He obtained the same solution for the case of an instantaneous lumped source, and also solved a number of other specific problems.

§ 3. Peculiarities of Propagation of Heat During Linear and Nonlinear Thermal Conduction

The basic features of the process of nonlinear thermal conduction and the peculiarities distinguishing it from the process of linear thermal conduction, are best of all clarified in an example of the problem about propagation, in an unlimited initially cold medium, of heat from an instantaneous plane source of energy. Let us assume that at initial moment $t = 0$ in plane $x = 0$, there was released energy $\mathcal{E}$ per 1 cm^2 of surface ($\mathcal{E}$ in erg/cm^2). In subsequent moments the heat spreads to both sides from plane $x = 0$.

The heat-conduction equation (10.10) for the considered problem has the form

$$\frac{\partial T}{\partial t} = \frac{\partial}{\partial x}\chi\frac{\partial T}{\partial x}, \qquad (10.18)$$

where the distribution of temperature in space obeys the condition of conservation of energy

$$\int_{-\infty}^{\infty} T\,dx = Q. \qquad (10.19)$$

Magnitude Q is equal to $\mathcal{E}/\rho c_p$ if the process occurs at constant pressure, and $\mathcal{E}/\rho c_V$ if specific volume is constant.

In this case two equations, (10.18) and (10.19), are equivalent to one heat-conduction equation (10.10) with a delta-shaped source (both with respect to time and coordinate):

$$q(x, t) = Q\delta(x)\,\delta(t).$$

At initial moment $t = 0$ the temperature of the medium is considered to be identically equal to zero everywhere except the point where the energy release took place:

$$T(x, 0) = Q\delta(x).$$

Solution of the problem on hand in the case of linear thermal conduction χ = const is well-known. It is given by the expression

$$T = \frac{Q}{\sqrt{4\pi\chi t}}\,e^{-\frac{x^2}{4\chi t}}. \qquad (10.20)$$

A characteristic property of linear thermal conduction consists in that the heat is concentrated at the point of energy release only in initial moment $t = 0$ (when $x = 0$, $T \to \infty$ as $t^{-1/2}$). In subsequent moments of time the heat instantly spreads to all the space and the temperature tends to zero for infinity, when $x \to \pm\infty$, only asymptotically. Basic energy content is concentrated in the region with dimensions of the order $x \sim \sqrt{4\chi t}$, which grows with the passage of time in proportion to $\sqrt{t}$. Correspondingly, as $1/\sqrt{t}$ and temperature drops, the full quantity of heat, proportional to $\int T\,dx \sim Tx \sim \frac{1}{\sqrt{t}}\sqrt{t} \sim 1$, remains constant. Distribution of temperature in consecutive moments of time are shown in Fig. 10.1.

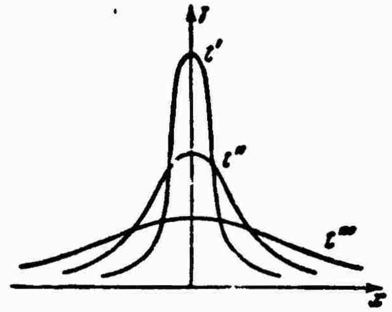

Fig. 10.1. Propagation of heat from an instantaneous plane source during linear thermal conduction.

The asymptotic character of decrease of temperature to infinity and the instantaneous character of propagation of heat to an unlimited distance within the scope of the thermal conduction theory is connected with the finite character of the coefficient of thermal conduction at zero temperature.

Practically, of course, at a large distance to a given moment of time there penetrates only an insignificantly small quantity of heat; the law of drop of temperature to infinity is extremely sharp, Gaussian; however, in principle, at any, no matter how long, but finite distance from the source, the temperature immediately after the moment of energy release is finite. It is necessary to note that the Gaussian law of temperature dropping to infinity is connected with the approximate description of propagation of heat within the scope of the thermal conduction theory. In reality, at long distances the temperature is determined not by the diffusion of "hot" molecules from a heated region (in a gas), but by direct, "straight-through" molecules, falling from a heated region at long distances, not experiencing any collisions. Therefore, in reality, to infinity the law of drop of temperature is not Gaussian (10.20), but only exponential, $T \sim e^{-x/l_a}$, where l_a is the range of a molecule. It is clear that with any preexponential factor, in a given moment of time, the simple exponential $\exp(-x/l_a)$ finally will become larger than the Gaussian exponential $\exp(-x^2/4\chi t)$ ($\chi = l_a\bar{v}/3$). However, in this region at large distances there is such an insignificant quantity of heat that consideration of it does not present any interest.

We shall check the assumption on the possibility of disregarding the motion of the substance.

If the medium is gas, from the place of energy release (in this case from plane x = 0) there spreads a compressional wave (or shock wave). The speed of its propagation through an undisturbed substance is of order of the speed of sound in a heated region, i.e., of the order of the thermal velocity of heated molecules $\overline{v}$. Speed of propagation of heat by means of thermal conduction

$$\frac{dx}{dt}\Big|_{,} \sim \frac{d}{dt}\sqrt{\chi t} \sim \sqrt{\frac{\chi}{t}} \sim \frac{\chi}{x} \sim \frac{l_a}{x}\overline{v},$$

i.e., as soon as the heat spreads to a distance longer than the mean path of the molecules, the speed of thermal conduction becomes less than the speed of hydrodynamic conduction. Inasmuch as in general there is no meaning to consider distances less than the path of molecules, one may assume that the heat spreads always with subsonic speed. If the quantity of released energy is small and the compressional wave weak, the speed of the substance is small as compared to the speed of sound. It is possible to consider, as this was noted from the very beginning, that the role of hydrodynamics reduces simply to the equalization of pressure, and the process of propagation of heat occurs at constant pressure.

If, however, the energy release is great and the compressional wave, going a considerable distance from the place of energy release, is a shock wave, then we are dealing with a purely hydrodynamic process of a severe explosion, which was considered in § 25 of Chapter I; the role of thermal conduction of the substance in the propagation of energy turns out to be immaterial.

Let us now assume that the coefficient of thermal conduction depends on temperature, where by it decreases with the drop of temperature and turns into zero at zero temperature, like this takes place during radiant thermal conduction. In this case the heat cannot instantly penetrate to any great distances, but spreads from the source with terminal velocity in such a way that there exixts a clear boundary separating the heated region from the cold, to which thermal perturbation did not yet arrive. Heat spreads from the source in the form of a wave, the front of which is the shown boundary surface. Such a wave is called thermal. Distribution of temperature in a thermal wave in consecutive moments of time is schematically shown in Fig. 10.2.

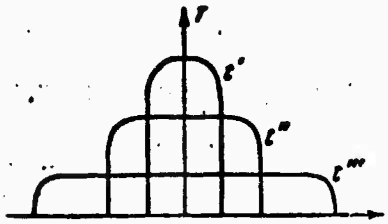

Fig. 10.2. Propagation of a thermal wave from an instantaneous plane source.

In a cold undisturbed medium the temperature and flux of heat are equal to zero, inasmuch as the coefficient of thermal conduction reverts to zero. By virtue of continuity, the flow on the front of the wave also turns into zero. In linear thermal conduction, when x = const, the return to zero of the heat flux can be connected only with the disappearance of gradient of temperature. In nonlinear thermal conduction with coefficient diminishing to zero when $T \to 0$, the flux can also disappear when the gradient of temperature differs from zero, only at the expense of return of the thermal conduction coefficient to zero. This circumstance in particular is also connected with the appearance of a sharp front of a thermal wave.

In order to explain what has been said, we will consider the layer near the front of a wave. If we limited ourselves to short periods of times, during which the wave spreads at distances that are small as compared to the size of the region enveloped by the wave, i.e., with coordinate of front x_f (see Fig. 10.2), during such time the speed of the front can approximately be considered as constant.

Distribution of temperature near the front can be found in the form of a stationary wave $T = T(x - vt)$, where v is the speed of the front. Profile of temperature near the front is quasi-stationary in the system of coordinates connected with the front.

Putting in equation (10.18) the solution in the form of $T = T(x - vt)$, we obtain, for the profile of temperature near the front, the equation

$$-v\frac{\partial T}{\partial x}=\frac{\partial}{\partial x}\chi\frac{\partial T}{\partial x}. \qquad (10.21)$$

Considering $\chi = aT^n (n > 0)$ and integrating this equation twice with boundary condition $T = 0$ when $x = x_f$, we obtain the profile of temperature:

$$T=\left[\frac{nv}{a}\left|x_ф-x\right|\right]^{\frac{1}{n}}. \qquad (10.22)$$

it is also shown schematically in Fig. 10.2.

Coordinate of front x_f and speed of front $v = \frac{dx_f}{dt}$ in this formula are indefinite functions of time. They are found by means of solution of the entire problem for the whole space.

The fact that the temperature returns to zero according to law (10.22) also confirms the accuracy of the affirmation about the existance of the sharp boundary of the heated region, i.e., the front of the thermal wave. If index $n \leq 0$, the coefficient of heat transfer χ, does not return to zero when $T = 0$, and equation (10.21) does not have solutions returning to zero at a finite distance, which corresponds to the instantaneous character of propagation of heat at any large distances.

From formula (10.22) it follows that the gradient of temperature near the front of a thermal wave is proportional to $dT/dx \sim$ $\sim |x_f - x|^{\frac{1}{n} - 1}$.

If $n > 1$, the gradient of temperature on the front (when $x = x_f$) returns to infinity, i.e., the front is steep. If $n < 1$, $(dT/dx)_{x_f} =$ $= 0$. The flux is always equal to zero when $x = x_f$: $S \sim T^n dT/dx \sim$ $\sim |x_f - x|^{\frac{1}{n}} \to 0$ when $n > 0$.

In §§ 12 and 17 of Chapter VII, in examining the structure of the front of a shock wave, taking into account the electron and radiant thermal conduction, it was shown, as in front of a shock wave which is spreading through a gas, there breaks loose a "tongue" of heat due to thermal conduction.

Profile of temperature in front of the shock is described by formula (10.22) (if motion of gas in front of shock can be disregarded), where speed v is the speed of the front of the shock wave. The profile has the form shown in Fig. 10.3a. A "tongue" breaks loose at a fully defined, finite distance $\Delta x = x_f - x_1$ (Fig. 10.3a), which depends on the temperature on the shock wave T_1

$$T_1 = \left(\frac{nv}{a}\Delta x\right)^{\frac{1}{n}}, \quad \Delta x = \frac{aT_1^n}{nv} = \frac{\chi(T_1)}{nv} = \frac{\chi_1}{nv}.$$

In the case of linear thermal conduction $\chi = \text{const}$, the "tongue" of heat spreads an infinitum, although its effective width is finite and is constant (at constant speed of shock wave). Solution of equation (10.21) when $\chi = \text{const}$ has in this case the form

$$T = T_1 e^{-\frac{x-x_1}{\Delta x'}}, \quad \Delta x' = \frac{\chi}{v}.$$

Profile of temperature in a heated layer is shown in Fig. 10.3b. As was already noted, the temperature returns to zero only at infinity.

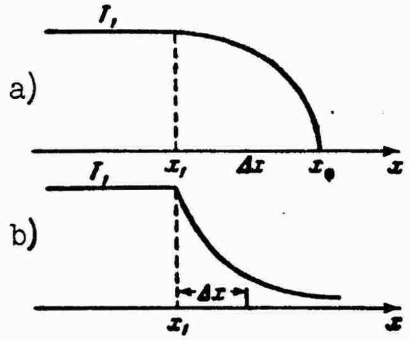

Fig. 10.3. Thermal conduction heating in front of a shock wave.
a) during nonlinear thermal conduction; b) during linear thermal conduction.

In molecular thermal conduction the law of drop of temperature to infinity due to the "straight-through" molecules differs from that which is dictated by the thermal conduction theory, not taking into account the motion of separate molecules. Similar to this, during heat transfer by radiation, the profile of the thermal wave near its boundary has the form of (10.22) only within the scope of the approximation of radiant thermal conduction. If we consider the existence of "straight-through" quanta, i.e., nonequilibrium of radiation of front edge of wave, we will arrive at the exponential law of drop of temperature on the front edge of a thermal wave: $T \sim e^{-x/l}$, where l is the range of radiation. This effect was studied in detail in § 3 of Chapter VII in examining the structure of the front of a shock wave taking into account the transfer of radiation.

Till now we considered propagation of heat in a medium with zero initial temperature. If $T_0 \neq 0$, the coefficient of nonlinear thermal conduction in an undisturbed substance is finite and the law of drop of temperature is different than (10.22); however, practically, at small initial temperatures the coefficient of radiant thermal conduction when $T = T_0$ is so small that this effect can be disregarded. Much more essential is the above-noted nonequilibrium of radiation on the front edge of a thermal wave, which leads to an exponential decrease of temperature $T \sim e^{-x/l}$ instead of root law (10.22).

Let us note one more essential distinction of nonlinear thermal conduction from linear. In the linear case there is the principle of superposition. If there is a totality of sources of energy, the heat from each of them spreads in an absolutely independent form. Solution of the equation of thermal conduction in the presence of extended sources is possible to present in the form of an integral "with respect to sources" from solutions corresponding to concentrated sources. In nonlinear thermal conduction the principle of superposition is incorrect. Propagation of heat from one source depends on the temperature to which the medium is heated at the expense of thermal perturbation coming from another source. In the general case of extended sources the solution is impossible to present in the form of an integral with respect to sources.

§ 4. Law of Propagation of a Thermal Wave from an Instantaneous Plane Source

The law of propagation of heat from a source is easy to obtain even without an exact solution of the equation by means of estimating the order of the magnitude of characteristic dimension of the heated region, or from dimension considerations. Problems about the propagation of heat from an instantaneous source (flat, point, filamentary) are solved exactly (see below). However, similar semiqualitative appraisals make the physical meaning of regularities very graphic and, furthermore, frequently are useful in the consideration of more complicated problems, for which exact solutions cannot be found.

Let us consider the propagation of heat from a plane instantaneous source. Results for the case of linear thermal conduction were already presented in the preceding paragraph, where an exact solution of the problem was given. In order to demonstrate the general trend of semiqualitative reasonings, we will repeat these results again.

Let us assume that the coefficient of thermal conduction is constant.

In equation (10.18) there enters one unique parameter, i.e., the coefficient of temperature transfer χ, cm^2/sec. The other measured parameter is energy per 1 cm^2: $\mathcal{E}$, erg/cm^2 of surface or magnitude Q, deg·cm. If x is the width of the region in which the basic quantity of heat is concentrated to moment t, from considerations of size it is clear that $x^2 \sim \chi t$, $x \sim \sqrt{\chi t}$. Speed of propagation of heat $\frac{dx}{dt} \sim \sim \sqrt{\frac{\chi}{t}} \sim \frac{\chi}{x} \sim \frac{x}{t}$. Average temperature in the heated region is of the order $T \sim \frac{Q}{x} \sim \frac{Q}{\sqrt{\chi t}}$. These simple results, which coincide in order of magnitude with the one that gives an exact solution of the problem (10.20), can be obtained directly from equation (10.18). Replacing in it the derivatives $\partial T/\partial t$, $\partial T/\partial x$ by ratios T/t, T/x, equal to them in order of magnitude, and replacing $\frac{\partial}{\partial x} \chi \frac{\partial T}{\partial x}$ by $\chi T/x^2$, we will arrive directly at the same regularities.

Let us now turn to the case of propagation of a nonlinear thermal wave. For the coefficient heat transfer we will take the exponential dependence $\chi = aT^n$, at which the heat-conduction equation has the form

$$\frac{\partial T}{\partial t} = a \frac{\partial}{\partial x} T^n \frac{\partial T}{\partial x}. \qquad (10.23)$$

In the equation there enters one parameter a cm^2/sec·deg^n. The other measured parameter is Q deg·cm. From them it is possible to compose one (independent) measured combination containing only length and time: aQ^n cm^{n+2} sec^{-1}. It follows from this the law of motion of the front of a thermal wave:

$$x_{\phi} \sim (aQ^n t)^{\frac{1}{n+2}} = (aQ^n)^{\frac{1}{n+2}} t^{\frac{1}{n+2}}.$$

Speed of propagation of a thermal wave is of the order

$$\frac{dx_{\phi}}{dt} \sim (aQ^n)^{\frac{1}{n+2}} t^{\frac{1}{n+2}-1} \sim \frac{x_{\phi}}{t} \sim \frac{aQ^n}{x_{\phi}^{n+1}}.$$

It is clear that with a large index n, the thermal wave is very quickly slowed down with respect to propagation. This is connected with the fact that during the propagation of heat the temperature drops and the coefficient of heat transfer decreases very sharply. Considering that average temperature in a thermal wave is of the order $T \sim Q/x_f$, and the mean coefficient of heat transfer $\chi = aT^n \sim aQ^n/x_f^n$, it is possible to write out the law of propagation of a thermal wave in a form corresponding to the linear theory: $x_f \sim \sqrt{\chi t}$. Here one should consider that the mean coefficient of heat transfer itself in this formula depends on time according to the law

$$\chi \sim \frac{aQ^n}{x_f^n} \sim \frac{aQ^n}{(aQ^n)^{\frac{n}{n+2}} t^{\frac{n}{n+2}}} = (aQ^n)^{\frac{2}{n+2}} t^{-\frac{n}{n+2}}.$$

The law of propagation of a thermal wave can also be obtained from the heat-conduction equation, replacing the derivatives approximately by ratios of magnitudes: $\partial T/\partial t \to T/t$; $\frac{\partial T}{\partial x} \to T/x_f$; $\frac{\partial}{\partial x} T^n \frac{\partial T}{\partial x} \to \to \frac{T^{n+1}}{x_f^2}$. We then obtain $x_f^2 \sim aT^n t \sim \chi t$; using the relationship $T \sim \sim Q/x_f$, we arrive at the already found laws.

§ 5. Self-Similar Thermal Wave from an Instantaneous Plane Source

Let us find an exact solution of a two-dimensional problem about the propagation of a thermal wave in an unlimited medium during instantaneous energy release at the time $t = 0$ in plane $x = 0$. The process is described by a nonlinear heat-conduction equation (10.23), where the solution satisfies the law of conservation of energy (10.19).

From the size considerations presented in the preceding paragraph, it is clear that the solution of the problem on hand is self-similar.* Really, the only dimensionless combination which can be composed from coordinate x, time t, and parameters of problem a and Q, is

$$\xi = \frac{x}{(aQ^n t)^{\frac{1}{n+2}}}. \tag{10.24}$$

Magnitude of dimension of temperature is $Q/(aQ^n t)^{\frac{1}{n+2}} = (Q^2/at)^{\frac{1}{n+2}}$. Therefore, the solution of $T(x, t)$ should be found in the form:

$$T = \left(\frac{Q^2}{at}\right)^{\frac{1}{n+2}} f(\xi), \tag{10.25}$$

where $f(\xi)$ is a new unknown function.

Putting expression (10.25) in equation (10.23) and passing to differentiation with respect to self-similar variable, with the help of formulas

$$\frac{\partial f}{\partial t} = -\frac{1}{n+2}\frac{df}{d\xi}\frac{\xi}{t}, \quad \frac{\partial f}{\partial x} = \frac{1}{(aQ^n t)^{\frac{1}{n+2}}}\frac{df}{d\xi}$$

we obtain an ordinary differential equation for function f:

$$(n+2)\frac{\partial}{\partial \xi}\left(f^n \frac{df}{d\xi}\right) + \xi\frac{df}{d\xi} + f = 0. \tag{10.26}$$

Solution of this equation should satisfy the conditions which follow from the physical conditions of the problem: $T = 0$ when $x = \pm\infty$ or: $T = 0$ when $x = \infty$ and $\frac{\partial T}{\partial x} = 0$ when $x = 0$ (by virtue of symmetry with respect to plane $x = 0$). Hence

$$f(\xi) = 0 \text{ when } \xi = \infty; \quad \frac{df}{d\xi} = 0 \text{ when } \xi = 0. \tag{10.27}$$

Solution of equation (10.26), satisfying conditions (10.27), was found in [1, 2]. It has the form

$$\begin{aligned} f(\xi) &= \left[\frac{n}{2(n+2)}(\xi_0^2 - \xi^2)\right]^{\frac{1}{n}} = \left[\frac{n}{2(n+2)}\xi_0^2\right]^{\frac{1}{n}}\left[1 - \left(\frac{\xi}{\xi_0}\right)^2\right]^{\frac{1}{n}} && \text{when } \xi < \xi_0, \\ f(\xi) &= 0 && \text{when } \xi > \xi_0. \end{aligned} \tag{10.28}$$

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*The concept of self-similarity, see Sections 11 and 25 in Chapter I. See also Chapter XII.

where ξ_0 is the constant of integration. Constant ξ_0 is found from the equation of conservation of energy (10.19), which takes on the form

$$\int_{-\infty}^{+\infty} f(\xi)\,d\xi = \int_{-\xi_0}^{+\xi_0} f(\xi)\,d\xi = 1. \qquad (10.29)$$

Calculation gives

$$\xi_0 = \left[\frac{(n+2)^{1+n}\,2^{1-n}}{n\pi^{\frac{n}{2}}} : \frac{\Gamma^n\left(\frac{1}{2}+\frac{1}{n}\right)}{\Gamma^n\left(\frac{1}{n}\right)}\right]^{\frac{1}{n+2}}. \qquad (10.30)$$

Law of motion of front of thermal wave $\xi = \xi_0$ is

$$x_\phi = \xi_0 (aQ^n t)^{\frac{1}{n+2}}. \qquad (10.31)$$

It, as one should have expected, with an accuracy of numerical coefficient ξ_0, coincides with the law found in the preceding paragraph from semiqualitative considerations.

Temperature in a plane thermal wave is conveniently expressed in the form

$$T = T_c\left(1 - \frac{x^2}{x_\phi^2}\right)^{\frac{1}{n}}, \qquad (10.32)$$

where $x_f(t)$ is the coordinate of the front, determined depending upon time by formulas (10.31) and (10.30), and T_c is the temperature in plane $x = 0$. It can be expressed through average temperature in the wave (average with respect to heated volume):

$$T_c = \frac{\overline{T}}{J}, \qquad (10.33)$$

where

$$\overline{T} = \frac{Q}{2x_\phi}; \quad J = \int_0^1 (1 - z^2)^{\frac{1}{n}}\,dz = \frac{\sqrt{\pi}}{n+2}\,\frac{\Gamma\left(\frac{1}{n}\right)}{\Gamma\left(\frac{1}{n}+\frac{1}{2}\right)}.$$

For instance, when $n = 5$, $\xi_0 = 0.77$ and $T_c = 1.12\overline{T}$.

In the calculation of variability of heat capacity the profile of temperature differs from (10.32) only very little. Actually, the profile of energy is

$$E = E_c\left(1 - \frac{x^2}{x_\phi^2}\right)^{\frac{1}{n'}}.$$

But $E \sim T^{1+k}$, $n' = (n - k)/(k + 1)$, whence

$$T = T_c \left(1 - \frac{x^2}{x_{\phi}^2}\right)^{\frac{1}{n-k}}.$$

Inasmuch as $n \sim 5$ and $k \sim 0.5$, this expression scarcely differs from (10.32) (in the first case the index $1/n = 1/5$; in the second, $\frac{1}{n - k} = 1/4.5$). The new constant $\xi_0(n')$ also hardly differs in the law of propagation of a thermal wave. The law of propagation itself changes more. When $n = 5$, $k = 0$ (constant heat capacity) $x_f \sim t^{1/7}$; when $n = 5$, $k = 0.5$ (i.e., $c_V \sim T^{0.5}$), $x_f \sim t^{\frac{1}{n'+2}} \sim t^{1/5}$.

Profile of temperature T/T_c depending upon x/x_f is depicted in Fig. 10.4a, for the case of $n = 5$. For a thermal wave with coefficient of thermal conduction strongly depending on temperature, the existence of a "plateau" of temperature is characteristic: temperature is almost constant and is equalized by thermal conduction in all the heated region, with the exception of the comparatively thin layer near the front, where it quickly drops to zero. Such a tendency is expressed more sharply the larger the index of nonlinearity n. Flux coordinate distribution is given by the expression

$$S \sim -T^n \frac{\partial T}{\partial x} \sim \left(1 - \frac{x^2}{x_{\phi}^2}\right)^{\frac{1}{n}} x.$$

Flux grows almost linearly from the beginning of $x = 0$ to the very edge of the wave and quickly drops to zero only near the edge, as shown in Fig. 10.4b. Divergence of flux $\partial S/\partial x$ is almost constant in all the region of the plateau. The main region of heated gas is cooled almost uniformly and only near the edge of the wave is the gas heated by the heat released from the main mass of gas (see Fig. 10.4c).

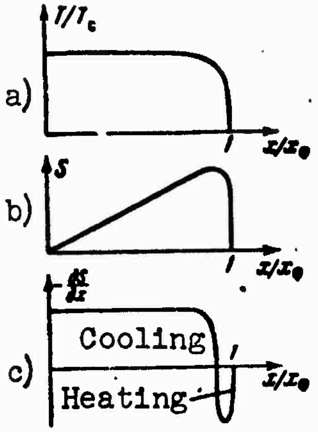

Fig. 10.4. Profiles of temperature, flux, and divergence of flux in a thermal wave.

The process of propagation of heat goes in such a way that the volume of heated gas is almost uniformly cooled and the energy lost by it is absorbed near the front of the wave, due to which the wave seizes all the new layers of cold gas.

Near the front the distribution of temperature can approximately be expressed in the form

$$T\sim\left(1-\frac{x^2}{x_\phi^2}\right)^{\frac{1}{n}}\sim\left[\frac{2}{x_\phi}(x_\phi-x)\right]^{\frac{1}{n}}\sim(x_\phi-x)^{\frac{1}{n}},$$

which was already found earlier (see formula (10.22)).

We shall direct in solutions (10.25), (10.28), and (10.30) the index n to the limit n → 0, which corresponds to the transition to linear thermal conduction (constant a in equation (10.23) in the limit n = 0 plays the role of a constant coefficient of heat transfer χ = const).

When n → 0, $\xi_0 \to 2/\sqrt{n}$

$$T=\frac{Q}{\sqrt{at}}[f(\xi)]_{n\to 0}=\frac{Q}{\sqrt{at}}\frac{1}{\sqrt{4\pi}}\left[\left(1-\frac{nx^2}{4at}\right)^{\frac{1}{n}}\right]_{n\to 0}=$$
$$=\frac{Q}{\sqrt{4\pi at}}e^{-\frac{x^2}{4at}},\quad a=\chi,$$

i.e., we arrive at the known solution of the linear heat-conduction equation (10.20).

In the conclusion of this paragraph let us note that a nonlinear second order equation (10.26) allows a transformation group, leaving the equation invariant. Actually, it is easy to check by direct substitution that if we introduce, instead of ξ and f, a new independent variable ξ' and f' by the formulas

$$\xi'=C^n\xi,\quad f'=C^2f,\quad C=\text{const},$$

in variables ξ' and f' the new equation will have the same form as (10.26). According to the Lie theorem, the order of an ordinary differential equation, allowing a one-parameter transformation group, can be lowered to one. For lowering the order it is convenient to introduce new variables:

$$y=\xi^{-\frac{2}{n}}f, \quad z=\ln\xi.$$

In these variables the new equation contains z only under the sign of the differential, so that it is possible to introduce a new variable p = dy/dz and exclude z, obtaining a first order equation in variables p and y:

$$y^n p\frac{dp}{dy}+np^2y^{n-1}+\frac{4+3n}{n}py^n+\frac{1}{n+2}p+\frac{4+2n}{n^2}y^{n+1}+\frac{y}{n}=0.$$

Consequently, the problem of solution of an equation of the second order (10.26) reduces to solution of an equation of the first order and a quadrature. Such a position is characteristic for many self-similar problems of the theory of nonlinear thermal conduction.*

§ 6. Propagation of Heat from an Instantaneous Point Source

Let us consider a spherically-symmetric problem. Let us assume that at the time t = 0 at point r = 0 energy $\mathcal{E}$ erg was released. The heat-conduction equation in this case has the form

$$\frac{\partial T}{\partial t}=\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\chi\frac{\partial T}{\partial r}\right). \qquad (10.34)$$

Law of conservation of energy gives

$$\int_0^\infty T4\pi r^2\,dr=\frac{\mathcal{E}}{\rho c_V}=Q \text{ deg}\cdot\text{cm}^3.$$

Solution of the problem for linear thermal conduction χ = const is known:

$$T=\frac{Q}{(4\pi\chi t)^{\frac{3}{2}}}e^{-\frac{r^2}{4\chi t}}. \qquad (10.35)$$

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*And also for self-similar problems of gas dynamics. For details see Chapter XII.

Heat spreads so that the basic energy is concentrated in a sphere, the radius of which is on the order of

$$r\sim\sqrt{4\chi t},$$

analogous to the plane case when $x \sim \sqrt{4\chi t}$. Temperature in the center drops as $T \sim Q/r^3 \sim Q/(\chi t)^{3/2}$.

These regularities follow directly from considerations of size; they can also be obtained by means of estimating from equations (10.34) and (10.35), if one were to replace the derivatives by ratios of magnitudes (see § 4).

Let us now consider the case of nonlinear thermal conduction with $\chi = aT^n$ and $n > 0$. The equation takes on the form

$$\frac{\partial T}{\partial t}=\frac{a}{r^2}\frac{\partial}{\partial r}\left(r^2T^n\frac{\partial T}{\partial r}\right). \tag{10.36}$$

Let us find the law of motion of the front of a thermal wave, just as in the plane case. We have

$$r_{\text{ф}}^2\sim\chi t,$$

where χ is the coefficient of heat transfer, corresponding to the average temperature of the heated region at the time t. But

$$T\sim\frac{Q}{r_{\text{ф}}^3}, \tag{10.37}$$

so that $r_f^2 \sim aT^nt \sim aQ^nr_f^{-3n}\, t$, whence

$$r_{\text{ф}}\sim(aQ^n)^{\frac{1}{3n+2}}\,t^{\frac{1}{3n+2}}. \tag{10.38}$$

Speed of the front of the thermal wave is proportional to

$$\frac{dr_{\text{ф}}}{dt}\sim\frac{r_{\text{ф}}}{t}\sim\frac{(aQ^n)^{\frac{1}{3n+2}}}{t^{\frac{3n+1}{3n+2}}}\sim\frac{aQ^n}{r_{\text{ф}}^{3n+1}}. \tag{10.39}$$

It extraordinarily sharply decreases with respect to propagation of the wave. For instance, when $n = 5$, $dr_f/dt \sim 1/r^{16}$. The exact solution of the heat-conduction equation is found in self-similar form

$$T=\left(\frac{Q^{\frac{2}{3}}}{at}\right)^{\frac{3}{3n+2}}\varphi(\xi), \tag{10.40}$$

where self-similar variable ξ is defined as

$$\xi = \frac{r}{(aQ^n t)^{\frac{1}{3n+2}}}. \qquad (10.41)$$

Putting (10.40) in equation (10.36), we obtain an ordinary equation for function $\varphi(\xi)$, somewhat differing from equation (10.26) for the plane case. This equation was solved by S. Z. Belen'kiy (deceased and independently by G. I. Barenblatt [2].*

The final solution can be written in a form similar to (10.32),

$$T = T_c \left(1 - \frac{r^2}{r_ф^2}\right)^{\frac{1}{n}}, \qquad (10.42)$$

where radius of the front

$$r_ф = \xi_1 (aQ^n t)^{\frac{1}{3n+2}}. \qquad (10.43)$$

Constant ξ_1 is equal to

$$\xi_1 = \left\{ \frac{3n+2}{2^{n-1} n \pi^n} \frac{\Gamma^n\left(\frac{5}{2} + \frac{1}{n}\right)}{\Gamma^n\left(1 + \frac{1}{n}\right) \Gamma^n\left(\frac{3}{2}\right)} \right\}^{\frac{1}{3n+2}}.$$

Temperature in center T_c is equal to

$$T_c = \frac{4\pi}{3} \xi_1^3 \left[\frac{n \xi_1^2}{2(3n+2)}\right]^{\frac{1}{n}} \bar{T}, \qquad (10.44)$$

where

$$\bar{T} = Q \Big/ \frac{4\pi}{3} r_ф^3$$

is the average volume temperature at the time when the front of the wave reached radius r_f.

For instance, when n = 5, $\xi_1 = 0.79$, and $T_c = 1.28\bar{T}$. With variable of heat capacity $c_V \sim T^{0.5}$ (k).5)

$$E = E_c \left(1 - \frac{r^2}{r_ф^2}\right)^{\frac{1}{n'}}, \quad T = T_c \left(1 - \frac{r^2}{r_ф^2}\right)^{\frac{1}{n-k}},$$

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*Propagation of a thermal wave, close to spherical, was considered by E. I. Andriankin and O. S. Ryzhov [3]. E. I. Andriankin [4] considers a spherical thermal wave taking into account the energy of radiation.

as also in the plane case. In the law of propagation of a thermal wave, instead of $r_f \sim t^{1/(3n+2)}$ we obtain $r_f \sim t^{1/(3n'+2)}$. When $n = 5$, $k = 0$, $r_f \sim t^{1/17}$, and $\frac{dr_f}{dt} \sim r_f^{-16}$; when $n = 5$, $k = 0.5$, $n' = 4.5$, and $r_f \sim t^{1/15.5}$, $\frac{dr_f}{dt} \sim r_f^{-14.5}$.

Distribution of temperature along the radius in a spherical case is precisely the same as in the plane case. The flux in almost all the region from the center and to the front grows linearly along the radius and only near the very front drops to zero:

$$S \sim -T^n \frac{\partial T}{\partial r} \sim \left(1 - \frac{r^2}{r_f^2}\right)^{\frac{1}{n}} r.$$

Divergence of the flux is almost constant in all the sphere with the exception of the thin layer near the front: volume of gas is cooled comparatively uniformly, sending energy which is absorbed near the front, and heating all the new layers of the substance.

Let us imagine that in a small volume of gas there occurred very fast release of a large energy content, as a result of which the substance was heated to a very high temperature. From the place of energy release through the surrounding gas spreads the thermal wave.

Speed of propagation of the thermal wave, according to formula (10.39), decreases with respect to distribution and drop of temperature of a heated sphere according to the law: $dr_f/dt \sim aQ^n/r_f^{3n+1}$. But $r_f \sim (Q/T)^{1/3}$, so that $dr_f/dt \sim aT^{n+1/3}\, Q^{-1/3}$. During radiant thermal conduction $n = 5$ and $dr_f/dt \sim T^{5.3}$. Speed of sound in a heated gas, roughly speaking, is proportional to $\sqrt{T}$. Consequently, if in the beginning the temperature is very high (is "infinite") the speed of propagation of thermal waves is certainly greater than the speed of sound. During propagation of a wave through a motionless cold gas of constant density, the pressure in it increases. Roughly speaking, the pressure behind the front of a thermal wave is proportional to temperature $p \sim \rho T$, so that the profile of pressure approximately coincides with the profile of temperature. The existence of a pressure gradient in the wave permits the gas to accelerate, scattering from center; its mass is redistributed, attempting to concentrate near the periphery, at the front of the thermal wave. Perturbations spread through the gas with the speed of sound. Therefore, in the beginning, while the thermal wave moves much faster, the substance behind it does not succeed to move noticeably. As we have seen, the thermal wave, with respect to propagation, is extraordinarily quickly slowed down. After a certain time its speed drops to a magnitude of the order of the speed of sound and then becomes less than it. From this moment the thermal conduction wave no longer overtakes the sound perturbations, the substance moves and there will form a shock wave which bursts forward, spreading in front of the thermal wave with a speed in order of magnitude coinciding with the speed of sound in the heated gas behind it. Gradually the process emerges into the conditions described by the solution of the problem about the powerful explosion (see § 25 of Chapter I). Thus, the moment of formation of the shock wave and its equalization in front of the thermal wave approximately coincides with the moment when the speed of the thermal wave drops to the speed of sound in the heated gas.

An estimate shows that in air of normal density this occurs when the temperature in the heated sphere drops to a magnitude of order of 300,000° K. If initial temperature of air at the time of energy release is much greater than this magnitude, there exists a clearly expressed stage on which the energy spreads through the motionless air by means of radiant thermal conduction in the form of a thermal wave. When temperature in the expanded heated sphere drops to ~300,000° K, there will form and burst forward a shock wave, and the role of radiant thermal conduction reduces exclusively to temperature balance in the central region.

If, however, concentration of energy in the beginning is such that the temperature of air is lower than 300,000° K, a thermal wave in general does not appear, and energy from the very beginning spreads by hydrohynamic means due to the shock wave.

At the end of § 3 we noted that the profile of temperature on the lower edge of a thermal wave coincides with the profile of temperature in the heating zone of a very strong shock wave (in a very strong shock wave ahead of the shock there bursts a "tongue" of heating by radiant thermal conduction). In particular, on the very front edge of the thermal wave radiation is unbalanced by the "straight-through quanta" and temperature drops to zero by exponential law depending upon the optical coordinate. This means that the visible surface brightness of the front of a thermal wave coincides with the surface brightness of the front of a very strong shock wave. In § 4 of Chapter IX we showed that this limiting brightness in air of normal density corresponds to effective temperature in the visible part of the spectrum, approximately 17,000° K. The same effective temperature is also possessed by the surface of the front of a thermal wave. Thus, observing a thermal wave from afar, spreading through air, we will "see" a temperature of the order of 17,000°, in spite of the fact that in the central regions of the wave the temperature can reach many hundreds of thousand degrees.

§ 7. Certain Self-Similar Two-Dimensional Problems

Let us consider several self-similar problems. Two of them we shall investigate by the semiqualitative method presented in § 4. For one we will obtain an exact solution.

Constant Temperature on Boundary

Let us assume that on the boundary of a plane half-space x = 0 with zero initial temperature there is maintained constant temperature T_0. From the boundary inside the medium there spreads a thermal wave as shown in Fig. 10.5. Inasmuch as there is a scale of temperature T_0, the coefficient of heat transfer in order of magnitude is equal to $\chi \sim aT_0^n$, and the front of the thermal wave is propagated according to the law

$$x_\phi \sim \sqrt{\chi t} \sim (aT_0^n t)^{\frac{1}{2}}.$$

The value of the numerical coefficient in this formula, just as the profile of temperature, which obviously, is self-similar, can be found by means of numerical integration of an ordinary differential equation for dimensionless function $f(\xi)$:

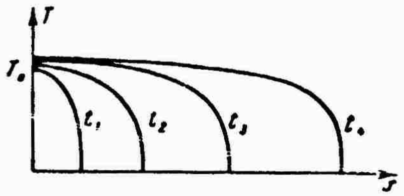

Fig. 10.5. Propagation of a thermal wave at assigned temperature on the boundary.

$$T = T_0 f(\xi), \quad \xi = \frac{x}{(aT_0^n t)^{\frac{1}{2}}}$$

under boundary conditions $f(0) = 1$, $f(\infty) = 0$.

The heat flux through the boundary decreases with the passage of time according to the law:

$$S \sim aT_0^n \frac{\partial T}{\partial x} \sim \frac{aT_0^{n+1}}{x_\phi} \sim \frac{aT_0^{n+1}}{(aT_0^n t)^{\frac{1}{2}}} \sim \frac{a^{\frac{1}{2}} T_0^{\frac{n+2}{2}}}{t^{\frac{1}{2}}}.$$

How the energy content in a thermal wave changes in time can be estimated by any of two methods:

$$\mathscr{E} \sim \int_0^{x_\phi} T\,dx \sim T_0 x_\phi \sim t^{\frac{1}{2}}, \qquad \mathscr{E} \sim \int_0^t S\,dt \sim \int_0^t \frac{dt}{t^{\frac{1}{2}}} \sim t^{\frac{1}{2}}.$$

Constant Flux on Boundary

Let us assume that on the boundary there is assigned a constant heat flux S_0, proceeding to the body from the outside:

$$S_0 = -\varkappa\left(\frac{\partial T}{\partial x}\right)_0 = -c_V\varrho a T^n \left(\frac{\partial T}{\partial x}\right)_0 = \text{const when } x = 0.$$

The law of propagation of a thermal wave and change of temperature in the wave in time will be found by replacing the derivatives with ratios of the magnitudes.

The flux in the zone of a thermal wave varies from S_0 to zero. Average temperature in the wave in order of magnitude is given by this relationship:

$$S_0 \sim c_V\varrho \frac{aT^{n+1}}{x_\phi}.$$

But from the heat-conduction equation it follows that in order of magnitude

$$\frac{T}{t} \sim \frac{S_0}{x_\phi}.$$

From these two approximate equations we will find the law of propagation of a thermal wave and the law of change of temperature in time:

$$x_\phi \sim (c_V\varrho a S_0^n)^{\frac{1}{n+2}} t^{\frac{n+1}{n+2}}, \quad T \sim \left(\frac{S_0^2}{c_V\varrho a}\right)^{\frac{1}{n+2}} t^{\frac{1}{n+2}}.$$

When $n = 5$ $x_f \sim t^{6/7}$, $T \sim t^{1/7} \sim x_f^{1/6}$, $\frac{dx_f}{dt} \sim t^{-1/7}$.

The speed of a thermal wave decreases very slowly and average temperature slowly increases. Temperature increase is explained by the fact that with respect to propagation of the wave the gradient of temperature decreases, and in order to support constancy of flux, the coefficient of thermal conduction should increase. Propagation of a wave is shown in Fig. 10.6.

Solution of the Dipole Type

Let us assume that near the plane boundary of a half-space in some layer there occurred an energy release. Let us assume that the heat spreads in the body so fast that the temperature on the boundary drops very quickly to a small magnitude, practically to zero. In spite of the fact that the temperature on the boundary is very small, the heat flux through the boundary remains finite (the gradient of temperature is correspondingly very great), so that energy flows from the body. In the problem there exists no integral of energy.

We idealize the problem on hand in order to exclude from it the dimensional parameters of length (for instance, thickness of layer, where the energy release occurred, or its distance from the boundary). We shall consider that the energy release happened instantly in an infinitely thin layer on the surface of the body x = 0, whereby in the limit, when the thickness of the layer of energy release tends to zero and the layer itself approaches the surface x = 0, there remains the final "moment" of temperature.

$$\int_0^\infty xT(x, 0)\,dx < \infty \quad \text{when} \quad T(x, 0) \to \delta(x).$$

It is easy to show that in this case under the condition that temperature on the boundary is equal to zero, instead of an integral of energy, as in the problem about the plane instantaneous source, there is an integral of "moment": the moment of temperature is kept in time. This position was established by G. I. Barenblatt [5].

We shall multiply by x the heat-conduction equation (10.23) and integrate from 0 to ∞, taking into account that there is no flux at infinity. Integrating by parts, we find

$$\frac{d}{dt}\int_0^\infty xT(x, t)\,dx = -\frac{a}{n+1}T^{n+1}(0, t).$$

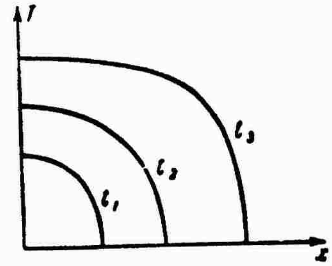

Fig. 10.6. Propagation of a thermal wave with a given flux on the boundary.

If on the boundary T(0, t) = 0, the moment is kept in time, and the "dipole moment" of temperature is retained:

$$\int_0^\infty xT(x,t)\,dx = P = \text{const.} \qquad (10.45)$$

The problem is then self-similar, since there are only two dimensional parameters, P deg·cm^2 and a cm^2 sec^{-1}deg^{-n}. It was solved by G. I. Barenblatt and Ya. B. Zel'dovich [6] in reference to the process of gas filtration. The front of a thermal wave spreads according to the law:

$$x_\phi = \xi_0 (aP^n t)^{\frac{1}{2(n+1)}}.$$

Temperature can be presented in the form

$$T = \left(\frac{P}{at}\right)^{\frac{1}{n+1}} M \left(\frac{x}{x_\phi}\right)^{\frac{1}{n+1}} \left[1 - \left(\frac{x}{x_\phi}\right)^{\frac{n+2}{n+1}}\right]^{\frac{1}{n}}, \qquad (10.46)$$

where numerical constants ξ_0 and M are equal to

$$\xi_0 = (n+2)^{\frac{1}{2}} (n+1)^{-\frac{n}{2(n+1)}} n^{-\frac{1}{2(n+1)}} 2^{\frac{1}{2(n+1)}} \left[B\left(1+\frac{1}{n}, \frac{n+1}{n+2}+1\right)\right]^{-\frac{n}{2(n+1)}},$$

$$M = \left[\frac{n}{2(n+2)}\right]^{\frac{1}{n}} \xi_0^{\frac{2}{n}}.$$

Here B(p, q) is the so-called beta function, for which there exist tables.

When n = 5 the function of temperature has the form

$$T \sim \frac{1}{t^{\frac{1}{6}}} \left(\frac{x}{x_\phi}\right)^{\frac{1}{6}} \left[1 - \left(\frac{x}{x_\phi}\right)^{\frac{7}{6}}\right]^{\frac{1}{5}},$$

and the front spreads according to the law

$$x_\phi \sim t^{\frac{1}{12}}, \quad \frac{dx_\phi}{dt} \sim \frac{1}{t^{\frac{11}{12}}} \sim \frac{1}{x_\phi^{11}}.$$

Propagation of a thermal wave is shown in Fig. 10.7.

It is easy to see that the flux through boundary x = 0 is different than zero, i.e., energy flows from the medium. Actually, when

$x/x_f \leq 1$

$$T \sim \left(\frac{x}{x_\phi}\right)^{\frac{1}{n+1}},$$
$$S \sim T^n \frac{\partial T}{\partial x} \sim \frac{\partial T^{n+1}}{\partial x} \sim \frac{\partial}{\partial x}\left(\frac{x}{x_\phi}\right) \neq 0. \qquad (10.47)$$

In his work [2] G. I. Barenblatt investigated a whole class of self-similar solutions of two-dimensional problems with very general conditions on the boundary of half-space:

$$T = \text{const}\, t^q, \qquad q > 0$$

or

$$S = \text{const}\, t^q, \qquad q > 0.$$

(temperature of flux on boundary increase in time by root law). They also considered problems with cylindrical and spherical symmetries.

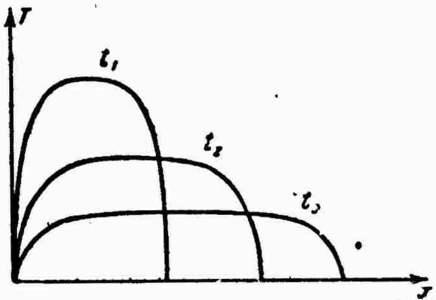

Fig. 10.7. Solution of the dipole type.

§ 8. Remarks on the Penetration of Heat into a Medium in the Calculation of Motion

Above it was noted that the possibility of disregarding the motion of a medium in examining thermal waves is connected with the fact that at an early stage of propagation of a thermal wave from a source, at a very high temperature, the speed of propagation is much greater than the speed of sound and the substance simply will not "shift from place."

In certain cases, however, the motion of a medium turns out to be essential from the very beginning.

Let us assume that the temperature on the boundary of a medium grows with the passage of time by root law $T_0 = \text{const}\, t^q (q > 0)$.

The distance at which the heat penetrates the medium by the mechanism of radiant thermal conduction is proportional to

$$x_\phi \sim \sqrt{\chi t} \sim T^{\frac{n}{2}} t^{\frac{1}{2}} \sim t^{\frac{nq+1}{2}}, \; (\chi \sim T^n). \qquad (10.48)$$

Speed of propagation of a thermal wave is proportional to

$$\frac{dx_\phi}{dt} \sim \frac{x_\phi}{t} \sim t^{\frac{nq-1}{2}}.$$

A shock wave from an energy source on the boundary of a medium spreads in the depth of the medium with a speed of order of the speed of sound in a heated substance:

$$D \sim \sqrt{T} \sim t^{\frac{q}{2}}.$$

Let us compare the speeds of propagation of thermal and shock waves $\frac{dx_f}{dt}$ and D. If $\frac{nq - 1}{2} < \frac{q}{2}$, $q < \frac{1}{n - 1}$, in the beginning of the process, when $t \rightarrow 0$, the speed of the thermal wave is always greater than the speed of the shock wave, and the thermal wave overtakes the shock wave. In this stage the motion of the medium can be disregarded, as this was done above. Only starting from a certain moment t', when speed D becomes greater than $\frac{dx_f}{dt}$, the shock wave will burst forward, overtake the thermal wave, and the substance in the region of the thermal wave will move (of course, a clear time boundary t' does not exist, and the process of "acceleration" of the substance occurs gradually; t' constitutes an effective boundary between the two stages).

If $\frac{nq - 1}{2} > \frac{q}{2}$, $q > \frac{1}{n - 1}$, the position is the reverse: when $t \rightarrow 0$, $D > \frac{dx_f}{dt}$, the shock wave overtakes the thermal wave, and the thermal wave from the very beginning of the process spreads through the moving substance. Starting from a certain "effective" moment t'', the thermal wave bursts in front of the shock wave and spreads through the motionless medium. The mass of substance, enveloped by motion, which is proportional to $Dt \sim t^{\frac{q}{2} + 1}$ (per 1 cm^2 of surface), then composes an ever smaller fraction from the mass heated by the thermal wave, which is proportional to $x_f \sim t^{\frac{nq+1}{2}}$.

In an intermediate case $\frac{nq-1}{2} = \frac{q}{2}$, $q = \frac{1}{n-1}$, the speeds of propagation of thermal and shock waves grow with the passage of time by identical law. In general, there do not exist clearly expressed stages, when energy penetrates the medium only by one method (either by hydrodynamic means, or by means of thermal conduction), as in extreme cases $q \lessgtr \frac{1}{n-1}$. The substance is heated by thermal conduction and moves almost simultaneously.

It is remarkable that in the particular case of $n = 6$ (when the range of radiation is $l \sim T^3$) the equations of hydrodynamics, taking into account radiant thermal conduction (but without taking into account energy and radiation pressure), allow a self-similar solution. This solution corresponds to the law of build-up of temperature on the boundary of a medium $T_0 \sim t^{1/5}$ (the existence of such a self-similar solution is shown by Marshak [7]). Scale of density is constant in this case and is equal to the initial density of the medium ρ_0, pressure $p \sim \rho T \sim t^{1/5}$, and speed of the substance $u \sim \sqrt{p/\rho} \sim \sim t^{1/10}$.

The boundary coordinate of the perturbed region (front of a thermal or shock wave) grows with the passage of time according to the law

$$x \sim ut \sim \sqrt{\chi t} \sim \sqrt{T^6 t} \sim t^{\frac{11}{10}}. \tag{10.49}$$

A self-similar variable is the combination $\xi = \text{const}\, x t^{-11/10}$, so that the solution of the equations is in the form of

$$T = \text{const}\, t^{\frac{1}{5}} f_1(\xi), \quad u = \text{const}\, t^{\frac{1}{10}} f_2(\xi) \text{ and etc.}$$

It is essential that the self-similar solution be possible with an arbitrary law of dependence of thermal conduction (range of radiation) on density: $\chi = f(\rho)T^6$ (since the scale of density does not depend on time).

The fact that the equations of gas dynamics, taking into account radiant thermal conduction, indeed allow the shown self-similar solution, can easily be checked by means of direct consideration of these equations.*

The character of the self-similar mode depends on which is greater: the speed of sound $c \sim \sqrt{T}$ or the speed of propagation of perturbations by means of thermal conduction $x \sim \sqrt{\chi t}$. Both magnitudes grow in time by identical law $t^{1/10}$ and their relationship is determined by proportionality factors. Therefore the character of the process depends on the numerical value of the coefficient in the law of build-up of temperature on the boundary of a medium with the passage of time $T_0 \sim t^{1/5}$. Such a mode is possible in which through an undistrubed substance there runs a forward shock wave, and behind it through a heated and compressed substance follows a thermal wave. A mode is possible when the boundary between undisturbed and disturbed regions is the front of a thermal wave, behind which the substance is set into motion.

Let us note the work of I. V. Nemchinov [8], in which he considers certain problems of heat transfer by radiation taking into account the motion of the medium.

§ 9. Self-Similar Solution as a Limiting Solution of a Nonself-Similar Problem

Self-similar solutions are interesting not so much as particular solutions of separate narrow classes of problems, but mainly as limits,

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*Let us recall that the equations of continuity and motion in the calculation of radiant thermal conduction do not change, and in the equation of energy there is introduced an additional energy flow (10.8) (see § 9 of Chapter II).

toward which the solutions of more general problems not self-similar in their formulation asymptotically tend. This question was investigated by Ya. B. Zel'dovich and G. I. Barenblatt [9] in reference to a Cauchy problem for a nonlinear heat-conduction equation in a one-dimensional plane case (10.23).

The basic physical peculiarities of asymptotic behavior of a solution is most conveniently explained in an example of linear thermal conduction, when the solution is especially simple. Let us assume that at initial moment t = 0 there is assigned a distribution of temperature along axis x: $T(x, 0) = T_0(x)$, where the temperature is different than zero only on the final segment of axis x.*

As is known, the solution of the equation of thermal conduction (10.18) in this case has the form (χ = const):

$$T(x, t) = \frac{1}{\sqrt{4\pi\chi t}} \int_{-\infty}^{\infty} T_0(y)\, e^{-\frac{(x-y)^2}{4\chi t}}\, dy. \tag{10.50}$$

It constitutes a generalization of solution (10.20) in the case of a distributed source.

Let us consider the behavior of temperature when t → ∞ at large distances from the place where the heat was concentrated in the initial moment, i.e., when $x \gg y$. Expanding the nucleus of the integrand expression in a series with respect to powers of small magnitude y/x, we obtain

$$T(x, t) = \frac{1}{\sqrt{4\pi\chi t}}\, e^{-\xi^2} \Big[\int_{-\infty}^{\infty} T_0(y)\, dy + \frac{\xi}{\sqrt{\chi t}} \int_{-\infty}^{\infty} T_0(y)\, y\, dy + \frac{2\xi^2 - 1}{4\chi t} \int_{-\infty}^{\infty} T_0(y)\, y^2\, dy + \dots \Big]. \tag{10.51}$$

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*Such an initial condition is set up in reference to the problem about nonlinear thermal conduction. In the linear case the more general condition of sufficiently fast decrease of temperature to infinity is permissible.

where

$$\xi=\frac{x}{\sqrt{4\chi t}}.$$

The solution is in the form of the sum of self-similar terms, in which the time exponents each time increase by 1/2, and the coefficients are expressed through consecutive moments of the function of initial distribution of temperature. In the limit $t \to \infty$ the first member remains in the bracket, corresponding to solution (10.18) for a lumped source, where the following member of the expansion, which characterizes the distinction of the true solution from the limiting one, is on the order of $1/t^{1/2}$ with respect to the main one:

$$T=T_{\text{пред}}\left[1+\frac{\varphi(\xi)}{t^{\frac{1}{2}}}+\ldots\right]. \tag{10.51'}$$

Owing to the fact that equation (10.18) allows arbitrariness in the selection of origins coordinate and time reading and the scale of temperature (allows transformation groups $x' = x - x_0$, $t' = t + \tau$, $T' = kT$), equation (10.18) is satisfied more generally than (10.20), a self-similar solution of the form

$$T_{\text{авт}}(x-x_0,\ t+\tau,\ Q)=\frac{Q}{\sqrt{4\pi\chi(t+\tau)}}e^{-\frac{(x-x_0)^2}{4\chi(t+\tau)}}. \tag{10.52}$$

This solution corresponds to the instantaneous release of a defined quantity of heat $E = c_V\rho Q$ at point $x = x_0$ at the time $t = -\tau$.

It is easy to check that by means of corresponding selection of parameters x_0, τ, and Q it is possible to achieve that a self-similar solution of the type (10.52) better describs the exact solution (10.51) than self-similar solution (10.20), in which $x_0 = 0$, $\tau = 0$.

Actually, we will expand function (10.52) in powers of small magnitudes x_0/x and τ/t (in the limit $t \to \infty$, $x \to \infty$). By means of comparison of the expansion with exact solution (10.51) we see that if we select the values of Q, x_0, and τ equal to

$$Q = \int_{-\infty}^{\infty} T_0(y)\,dy,$$

$$\left.\begin{aligned} x_0 &= \frac{\int_{-\infty}^{\infty} T_0(y)\,y\,dy}{\int_{-\infty}^{\infty} T_0(y)\,dy}, \\ \tau &= \frac{\int_{-\infty}^{\infty} T_0(y)\,y^2\,dy}{\chi \int_{-\infty}^{\infty} T_0(y)\,dy}, \end{aligned}\right\} \qquad (10.53)$$

the members of the order of $t^{-1/2}$ and t^{-1} in brackets (10.51) disappear, so that

$$T(x, t) = T_{\text{self}}(x - x_0,\ t + \tau,\ Q)\left[1 + \frac{\psi}{t^{\frac{3}{2}}} + \dots\right]. \qquad (10.54)$$

The second member in brackets is of a higher order of smallness when t → ∞ than in expression (10.51').

The physical cause of the best coincidence of self-similar solution (10.52) with the exact solution consists in that, the self-similar solution (10.52) corresponds to instantaneous release of the very same quantity of heat at point x_0, which is the "center of gravity" $\bar{x}$ of the initial distribution of temperature $T_0(x)$. The moment of release exactly corresponds to the time, necessary for the heat to spread by means of thermal conduction from point $x = 0$ to the "center of gravity" $\bar{x} = x_0$. "Effective" quantity of heat $E = c_V \rho Q$ in the improved self-similar solution (10.52) turned out to be exactly equal to the actual quantity of heat $c_V \rho \int_{-\infty}^{\infty} T_0(x)\,dx$.

Analogously we can find a self-similar solution which in the best form nears the exact solution with distributed sources of heat in the case of nonlinear thermal conduction.

The self-similar solution of equation (10.23), corresponding to instantaneous liberation of heat at point $x = 0$ at the time $t = 0$, as described in § 5 (formulas (10.32), (10.33), (10.31), and (10.30)). In [9], in which it is possible to become familiar with the mathematical side of the investigation, it is shown that by means of a corresponding coordinate and time shift, i.e., selection of x_0 and τ, it is possible that the self-similar solution $T(x - x_0, t + \tau, Q)$ will differ from the exact one $T(x, t, Q)$ by members of a higher order than $t^{-\frac{2n+3}{n+2}}$.

§ 10. Concerning Heat Transfer by Unbalanced Radiation

Let us imagine that in rarefied air there was formed a spherical region with very high temperature T, so high that the mean path of radiation $l(T)$ is much greater than the radius of the sphere R and the heated sphere is transparent for radiation .* Highly-heated air radiates like a volume radiator. Light quanta almost freely exceed the bounds of the sphere and are absorbed in the surrounding layer of colder opaque air. Air in the sphere is cooled by the emission of light, and the surrounding cold layers are heated. The heated sphere is expanded, and the temperature in it drops: the process is very similar to the process of propagation of a thermal wave with the only difference that the radiation which transfers the energy is now essentially unbalanced.

There appears the question about with what speed is the heated sphere expanded. Such a problem was considered by A. S. Kompaneyets and Ye. Ya. Lantsburg [10]. Let us assume that the air in the sphere is heated to temperature T. If the sphere is transparent, the density of radiation in it in order of magnitude is equal to

$$U_1 = U_p(T)\frac{R}{l(T)} \ll U_p(T), \qquad (10.55)$$

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*Let us recall that range $l(T)$ quickly increases with increase of temperature: see § 2.

where $U_p(T) = 4\sigma T^4/c$ is the equilibrium density of radiation.

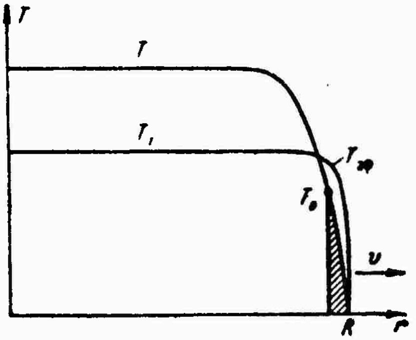

Fig. 10.8. Distribution of gas temperature and effective temperature of radiation in an unbalanced thermal wave.

Effective temperature of radiation in the sphere, determined by formula $U_1 = U_p(T_{ef})$, is less than the temperature of gas: $T_{ef} = T[R/l(T)]^{1/4}$. At the boundary of the sphere the temperature drops to zero (Fig. 10.8). Consequently, there exists a spherical surface where, decreasing with the drop of temperature, the range of radiation becomes comparable with radius R. Let us designate temperature in this point T_0:

$$l(T_0) \approx R. \tag{10.56}$$

A surface with temperature T_0 can be considered as the boundary between the internal, transparent region and the opaque external layer. On the boundary of transparency the density of radiation is still of the order U_1. However, it is higher than equilibrium density $U_p(T_0)$ just as in the outer-most layers: here the air absorbs radiation and is heated. Distribution of temperature and effective temperature, characterizing the density of radiation, is schematically shown in Fig. 10.8. Thickness of the layer, in which there occurs absorption of radiation and in which the temperature drops from the temperature of transparency T_0 to 0, is much less than radius R, since the range decreases quickly with lowering of temperature. This layer can be considered as plane and the state in it, in the system of coordinates connected with the layer, as quasi-stationary. For detecting the speed of propagation of the layer – the "front" of a thermal wave – one should consider the plane stationary mode, as done in Chapter IX in finding the speed of an air cooling wave by radiation. Speed of the wave v should depend only on the density of radiation U_1, supporting the propagation of the wave (or its effective temperature, which we for brevity will designate T_1) and temperature of transparency T_0 ($T_1 > T_0$). These magnitudes are determined by formulas (10.55) and (10.56).

Let us direct axis x in the direction of propagation of the wave and write out a system of equations. The equation of energy, on the assumption that heat capacity of gas is constant, has the form

$$-v\varrho c_v\frac{dT}{dx}+\frac{dS}{dx}=0.$$

The equation of radiation balance

$$\frac{dS}{dx}=c\,\frac{U_p(T)-U}{l(T)}, \quad U_p=\frac{4\sigma T^4}{c}.$$

In diffusion approximation

$$S=-\frac{lc}{3}\frac{dU}{dx}.$$

The system of course is fully analogous to the system describing a cooling wave (see Chapter IX). In front of the wave, in the area of cold air, T = 0, U = 0, S = 0. Behind the wave a condition is placed on the boundary of transparency: when $T = T_0$, $U = U_1$.

The system easily reduces to a nonlinear equation of the type dS/dU = f(S, U). The value of speed v is determined from the condition that the unknown integral curve passes through two end-points (S = 0, U = 0, and $S = S_0 = v\rho c_v T_0$, $U = U_1$; see Chapters IX, VII).

In [10] there are approximate expressions for speed in certain limiting cases.

1) If $T_1 - T_0 \ll T_1$, then

$$\beta=\frac{v}{c}=\frac{4}{\sqrt{3}}\frac{\gamma}{\sqrt{1+\gamma}}\left(\frac{T_1-T_0}{T_1}\right)^{\frac{1}{2}},$$

where $v = U_p(T_0)/\rho c_v T_0$ is the density ratio of radiation and gas energy at the temperature of transparency.

2) If $T_1 \gg T_0$, then

$$\beta = \frac{v}{c} = \frac{1}{\sqrt{3}} \frac{U_1}{\rho c_V T_0}.$$

By looking at this formula it can appear that at very large densities of unbalanced radiation the speed of a wave can increase without limit and even exceed the speed of light. In reality of course, such a situation is impossible. In a more exact description of equations of radiation transfer in diffusion approximation, taking into account the finiteness of the speed of light, the solution of the equation leads to the limited value of speed [11].

$$\beta = \frac{v}{c} = \frac{1}{\sqrt{3}} \frac{U_1}{U_1 + \rho c_V T_0}.$$

After we find the speed of the wave front $v(T_1, T_0)$, i.e., (U_1, T_0), we can find the law of expansion of the sphere $R(t)$, solving the system of equations

$$\frac{4\pi}{3} R^3 \rho c_V T = E, \quad \frac{dR}{dt} = v(U_1 T_0)$$

jointly with conditions (10.55) and (10.56), determining U_1 and T_0. Here E is the total energy of heated air, which obviously is constant.

Literature

1. Ya. B. Zel'dovich and A. S. Kompaneyets. Collection dedicated to the 70th birthday of A. F. Ioffe, 1950.

2. G. I. Barenblatt. Applied mathematics and mechanics, 16, 67 (1952).

3. E. I. Andriankin and O. S. Ryzhov. DAN SSSR, 115, 882 (1957).

4. E. I. Andriankin. ZhETF, 25, 428 (1958).

5. G. I. Barenblatt. Applied mathematics and mechanics, 18, No. 3, (1954).

6. G. I. Barenblatt and I. B. Zel'dovich. Applied mathematics and mechanics, 21, 718 (1957).

7. R. Marshak. Phys. Fluids., 1, 24 (1958). Translation: Problems of contemporary physics, No. 1 (1959).

8. I. V. Nemchinov. PMTF, No. 1, 36 (1960).

9. Ya. B. Zel'dovich and G. I. Barenblatt. DAN SSSR, 118, 671 (1958).

10. A. S. Kompaneyets and Ye. Ya. Lantsburg. ZhETF, 41, 1649 (1961).

11. A. S. Kompaneyets and Ye. Ya. Lantsburg. ZhETF, 43, 234 (1962).

CHAPTER XI

SHOCK WAVES IN SOLIDS

§ 1. Introduction

The study of the laws of propagation of shock waves in a condensed substance, i.e., in metals, water, etc, has a large theoretical and practical value. In particular, it is necessary for understanding and calculating explosive phenomena. Theoretical treatment of materials of these investigations gives us information about the equation of state of solids and liquids in the region of high pressures, which is very important for the solution of a large number of problems of geophysics, astrophysics, and other divisions of science.

For a description of hydrodynamic processes it is necessary to know the thermodynamic properties of the substance.

If for gases the calculations of thermodynamic functions do not cause large difficulties, the theoretical description of the thermodynamic properties of solids and liquids, at the high pressures which are developed in powerful shock waves, constitutes a very complicated problem, at present very far from its final solution. Therefore a special role is being obtained by experimental methods of investigation of a condensed substance in compressed state.

Until recently, physics of high pressures was limited to the study of a substance compressed in static conditions in piezometers of various design. In such a way, however, it is impossible, without the construction of huge installations, to compress a substance to pressures above a hundred thousand atmospheres and most of all, to ensure conditions for reliable measurements, since at higher pressures there starts to show up deformation of piezometric bombs, disturbing the carrying out of exact measurements of physical parameters. Meanwhile, contemporary science and technology is interested in pressures of hundreds of thousands and millions of atmospheres.

In the postwar years in the USSR and abroad there were offered completely different, dynamic methods of realization of high pressures and compressions, founded on the utilization of powerful shock waves. Shock waves were obtained and investigated in metals and other condensed bodies with pressures of hundreds of thousands and millions of atmospheres. In the USSR new methods were developed by L. V. Al'tshuler, S. B. Kormer, K. K. Krupnikov, B. N. Ledenev, A. A. Bakanova, M. V. Sinitsyn, A. I. Funtikov, V. I. Zhuchikhin, et al. [1-5], and in the United States by Walsh, Christian, Mallory, Goranson, Bankroft, McQueen, Marsh et al. [22-26].

Especially large successes in this direction were attained by Soviet scientists, who obtained record-breaking pressures of five million atmospheres (American authors studied shock waves of smaller intensity; work on the highest pressures attained by them, to two million atmospheres, were published later than the works of Soviet authors).

For the first time in human practice a solid was compressed two and more times; till now, so solid a substance could be "encountered" only in central regions of the globe and other cosmic bodies. These outstanding achievements in the area of obtaining high pressures and densities of solids permitted us to make a large number of extremely interesting conclusions concerning the thermodynamic behavior of a substance in such unusual conditions, and by semi-empirical means permitted the determination of important thermodynamic characteristics of strongly compressed metals.

The extraordinarily small duration of impact loads demanded the search for new methods of measurement, allowing the determination of physical parameters in conditions of a high-speed process, and the creation of appropiate instruments. A great contribution in this direction was made by Soviet researchers V. A. Tsukerman, G. L. Shnirman, A. S. Dubovik, P. V. Kevlishvili, Ye. K. Zavoyskiy et al. [6-12].

A basic characteristic feature, distinguishing a condensed state from a gaseous state and determining the behavior of solids and liquids during their compression by shock waves, is the strong interaction of atoms (or molecules) of the bodies with each other. The range of action of interatomic forces is very limited. It is on the order of the dimensions of the atoms and molecules themselves, i.e., on the order of 10^{-8} cm. In a sufficiently rarefied gas, where the average distances between particles are much greater than the dimensions of the particles, the interaction appears basically only at collisions, at the time of close approach of atmos or molecules.

Pressure in a gas has a thermal origin; it is connected with transfer of momentum by particles participating in thermal motion and always in proportion to temperature: $p = nkT$.

In order to strongly compress a gas, comparatively small pressures are required. The limiting compression of atmospheric gas in a shock wave of such amplitude can be considered just as strong.

Otherwise, a condensed substance behaves with respect to compression. In solids and liquids the atoms or molecules are at close distances from each other and strongly interact. This interaction in particular holds the atoms in the body. Forces of interaction have a double character. On the one hand, the particles, separated by a sufficiently large distance, are attracted to one another; on the other hand, upon closer approach, as a result of penetration of electron shells into each other, the atoms are repulsed. Equilibrium distances, at which the atoms of a solid are found in the absence of external pressure, correspond to the mutual compensation of attractive and repulsive forces, i.e., a minimum of potential energy of interaction. In order to separate atoms at large distances, it is necessary to surmount the adhesive forces and expend energy equal to binding energy, which for metals has an order of several tens or hundreds of kcal/mole (on the order of several ev/atom).* In order to compress a substance, it is necessary to surmount the repulsive forces which extraordinarily quickly increase with the approach of atoms. Compressibility of metals is equal by definition $\varkappa_0 = -\frac{1}{V} \cdot \frac{\partial V}{\partial p}$, and has under normal conditions an order of

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*Adhesive forces in solids are of various origin. In accordance with their nature, solids are usually subdivided into five groups: 1) ionic crystals, for instance NaCl, binding energy $U = 180$ kcal/mole; 2) crystals with covalent bond, for instance diamond, $U = 170$ kcal/mole; 3) metals, $U \sim 30\text{-}200$ kcal/mole; 4) molecular crystals connected by Vanderwaals forces, weak bond, for instance in CH_4 $U = 2.4$ kcal/mole; 5) crystals with hydrogen bonds, for instance ice, $U = 12$ kcal/mole. Here we will be basically interested in metals.

10^{-12} $cm^2/d \approx 10^{-6}$ atm^{-1}. In order to compress a cold metal by 10%, it is necessary to apply to it an external pressure of the order of 10^5 atm; compressibility usually decreases with the increase of pressure; for double compression of metals, pressures of the order of several million atmospheres are required.

Thus, during strong compression of a condensed substance, in it there is developed a colossal internal pressure, even in the absence of any heating, only by means of repulsion of atoms from each other. The existence of this pressure of a nonthermal origin, absolutely not peculiar to gases, and determines the basic peculiarities of behavior of solids and liquids during their compression by shock waves. In shock waves of very great amplitude, as we will see below, there also occurs strong heating of the substance, leading to the appearance of pressure, connected with thermal agitation of atoms (and electrons), which is called "thermal" in distinction from elastic, or "cold" pressure caused by repulsive forces. In principle, if the amplitude of a shock wave tends to infinity, the relative role of thermal pressure increases and in the limit the elastic pressure becomes small in comparison with thermal pressure; in waves of extraordinarily great amplitude solid matter initially behaves like a gas. However, in shock waves with pressures of a million atmospheres, obtained in laboratory conditions, pressures of both types are comparable with each other. In less strong waves, with pressure of the order of hundreds of thousands of atmospheres and below, elastic pressure predominates. The thermal energy of the substance compressed by the shock wave is also small in this case. All internal energy obtained by substance in the wave is expended in overcoming repulsive forces during compression of the body and is concentrated in the form of potential, elastic energy. The speed of propagation of small perturbations in a condensed substance, in distinction from gases, in no way is connected with temperature. It is determined by the elastic compressibility of the substance.

The numerical characteristic of "force" of the shock wave also changes. In gases, a measure of "force" of a wave is the ratio of pressures on both sides of the front. A limiting compression of several tens is attained when this ratio is equal to several tens or one hundred. The speed of propagation of the shock wave then considerably exceeds the speed of sound in the initial gas and the gas behind the front accelerates to speeds close to the speed of the shock wave. If the gas in the beginning was at atmospheric pressure, a shock wave with an amplitude of one hundred atmospheres is already "strong."

In a solid or liquid substance a shock wave with an amplitude of even one hundred thousand atmospheres is "weak." Such a wave hardly differs from an acoustic wave; it spreads with a speed close to the speed of sound, compresses the substance a total of several or tens of percent and imparts to it a speed behind the front, ten times less than the speed of propagation of the actual wave.

If we characterize the "force" of a shock wave by the ratio of its speed to the speed of sound in an undisturbed substance or by the proximity of compression to limiting compression, then for condensed bodies the "strong" waves are the ones with pressures not less then tens or hundreds of million atmospheres.

In this chapter we shall consider in detail the physical peculiarities of behavior of solids at high pressures and densities, we shall familiarize ourselves with the properties of shock compression, describe the experimental methods of the study of shock waves spreading in solids, and discuss the results obtained by these methods. We shall consider certain physical phenomena observed during the propagation of shock waves in metals and other bodies, and also during unloading of a substance after the exit of a shock wave to a free surface.

1. Thermodynamic Properties of Solids at High Pressures and Temperatures

§ 2. Compression of a Cold Substance

Pressure p and specific internal energy ε of solid matter can be divided into two parts. One of them, elastic components p_x, ε_x is connected exclusively with the forces of interaction effective between atoms of the body[*] and absolutely does not depend on temperature. The other, thermal components, is connected with heating of the body, i.e., with temperature. Elastic components p_x and ε_x depend only on density of the substance ρ or specific volume $V = 1/\rho$ and are equal to total pressure and specific internal energy at absolute zero temperature; that is why they are sometimes called "cold" pressure and energy.

In this paragraph we shall consider only the elastic members pressure and energy. Therefore we will assume that the body is at absolute zero temperature.

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[*] Here we will be basically concerned with metals which do do consist not of molecules, but atoms.

Mechanically, an equilibrium state of a solid at zero temperature and zero pressure* is characterized by mutual compensation of interatomic attractive and repulsive forces and a minimum of potential elastic energy, which can be taken as the origin of its reading $\varepsilon_x = 0$.**

We shall designate the specific volume of bodies in this state ($p = 0$, $T = 0$) through V_{0c}. This volume is somewhat less than volume V_0 under normal conditions ($p = 0$ or 1 atm, or all the same, $T_0 \approx \approx 300°$ K), since during heating of a substance from absolute zero to room temperature T_0 there occurs thermal expansion, which we will discuss in the following paragraph. Normal volume of metals V_0 is usually larger than volume V_{0c}, which we will call zero, by 1-2%. In many cases this small distinction of volumes V_0 and V_{0c} can be disregarded.

Considering here the behavior of solid matter during change of volume, we will bear in mind the inclusive compression (and expansion) of the body, detaching ourselves from the effects connected with anisotropy of elastic properties, deformation of shift, strength, etc, which appear at comparatively small pressures and compressions.

The curve of potential energy of a body, depending upon its specific volume V, qualitatively has the same character as the curve

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*Atmospheric pressure is insignificantly small as compared to the pressures appearing even at extraordinarily small changes of volume. Therefore it makes absolutely no difference whether the body is in a vacuum ($p_x = 0$) or at atmospheric pressure ($p_x = 1$ atm).

**At absolute zero temperature the atoms accomplish so-called zero-point oscillations, with which is connected energy $h\nu/2$ per one normal frequency oscillation ν. This energy can be included in potential energy $\varepsilon_x(V)$, so that ε_x is counted off from the level of zero-point oscillations in equilibrium state of the body when $p_x = 0$.

of potential energy of interaction of two atoms in a molecule depending upon the distance between nuclei. This curve is schematically depicted in Fig. 11.1. If volume V is greater than zero V_{0c}, the attractive forces predominate. The forces of interaction decrease quickly upon removal of atoms from each other; therefore with increase of volume, i.e., with dilution of atoms, the potential energy, increasing asymptotically, tends to a constant value of U, equal to the binding energy of atoms in the body.

U is the energy which must be expended in order to dilute all atoms of one gram of substance to "infinity"; it is approximately equal to the heat of evaporation of bodies (strictly speaking, it is equal to the heat of evaporation at absolute zero temperature). Heats of evaporation of metals usually have the order of several tens or hundreds of kcal/mole, i.e., several electron volts per atom.* Adhesive forces weaken at distances of order of the dimensions of an atomic cell, so that curve $\varepsilon_x(V)$ nears its asymptote $\varepsilon_x(V) \approx U$ upon expansion of the body to an order (with a double increase of the interatomic distance).

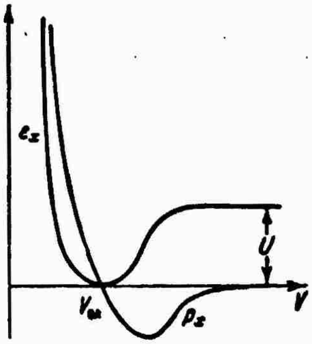

Fig. 11.1. Curves of potential energy and elastic pressure of a body depending upon specific volume.

During compression of a body a predominant role is played by the repulsive forces which sharply increase as they approach the atoms; therefore at volumes less than zero the potential energy $\varepsilon_x(V)$ rapidly increases. In order to imagine the speed of growth

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*For instance, in iron — 94 kcal/mole = 4.1 ev/atom = $= 6.96 \cdot 10^{10}$ erg/g. In aluminum — 55 kcal/mole = 2.4 ev/atom = $= 8.45 \cdot 10^{10}$ erg/g.

and order of magnitudes of energy, we will indicate that according to [1] the energy of cold compression of iron by 7% is $\varepsilon_x = 5.25 \cdot 10^8$ erg/g = 0.03 ev/atom, and in compression one and a half times it is ($V_0/V = 1.5$) - $\varepsilon_x = 2.42 \cdot 10^{10}$ erg/g = 1.4 ev/atom (pressures here are equal to $p_x = 1.31 \cdot 10^5$ atm and $p_x = 1.36 \cdot 10^6$ atm, respectively).

Elastic pressure is connected with potential energy by the relationship

$$p_x = -\frac{d\varepsilon_x}{dV}, \qquad (11.1)$$

which has a natural mechanical meaning (increase of energy is equal to the work of compression) and can be considered as an equation of the isotherm or adiabat of cold compression. Really, formula (11.1) follows from the general thermodynamic relationship $T\,dS = d\varepsilon + p dV$, if we consider that temperature T is equal to zero. But when T = 0 entropy S by the Nernst theorem is also equal to zero, i.e., it remains constant. Therefore isotherm T = 0 is simultaneously adiabat S = 0.

Pressure curve $p_x(V)$ also is schematically depicted in Fig. 11.1. At point $V = V_{0c}$ the elastic pressure is equal to zero; during compression the pressure rapidly increases, and during expansion it formally becomes negative.

Negative sign of pressure describes the physical fact that for expansion of a body from zero volume, responding to mechanical equilibrium when T = 0 and p = 0, to the body it is necessary to apply a tensile force. This force should surmount the adhesive forces that try to return the body to equilibrium volume V_{0c}.

In an experiment it is impossible to directly investigate the trend of the curve of cold expansion $p_x(V)$ when $V > V_{0c}$, since it is impossible to practically carry out strong extensive extension of a metal. The magnitude of negative pressures can be judged by the heat of evaporation of the substance. By definition, the area of the curve of cold expansion of a body from zero volume to infinity is equal to

$$\int_{V_{0к}}^{\infty} p_x(V)\,dV = -U. \qquad (11.2)$$

If the adhesive forces noticeably weaken during expansion of a body by approximately 10 times (increase of interatomic distance twice), the maximum magnitude of negative pressure has the order of $p_{max} \sim U/10V_{0c}$, which in iron for instance, is $p_{max} \sim 6 \cdot 10^{10}$ bar = $= 6 \cdot 10^4$ atm.*

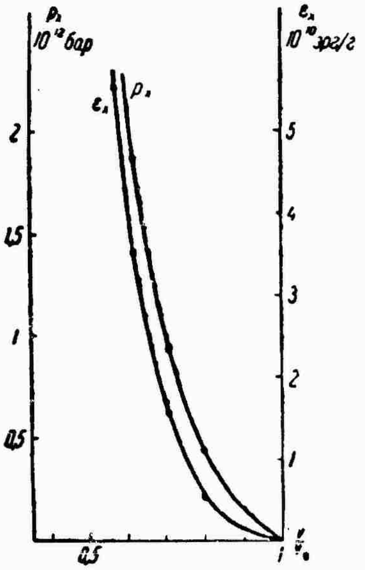

Fig. 11.2. Elastic pressure p_x and energy ε_x of iron (according to [1]).

The slope of the curve of elastic pressure at the point where pressure is equal to zero, corresponds to the compressibility of the substance determined in usual conditions (adiabatic compressibility only slightly differs from isothermal; when T = 0 they strictly coincide). Compressibility of iron

$$\varkappa_0 = -\frac{1}{V_0}\left(\frac{\partial V}{\partial p}\right)_{T_0} = 5{,}9 \cdot 10^{-13}\ \text{bar}^{-1},$$

whence

$$-V_{0к}\left(\frac{dp_x}{dV}\right)_{V_{0к}} \approx 1{,}7 \cdot 10^{12}\ \text{bar}.$$

Slope of the curve of cold compression determines the speed of propagation of elastic

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*This magnitude is much greater than the ultimate tensile strength of iron, which is usually on the order of 10^9 bar = 10^3 atm. The small magnitude of tensile strength is connected with the one-sided character of extension, with the existence of cracks in real metal, polycrystalline structure, etc.

waves in the body, i.e., the speed of "sound." Subsequently it will be shown that in a solid there exist several speeds of "sound." Meanwhile let us note that the speed of sound, defined by the usual method through compressibility $c_0 = V\left|\frac{\partial p}{\partial V}\right|_s^{1/2}$, is equal in iron at normal conditions to 5.85 km/sec.

Theoretical calculations of curves of cold compression $p_x(V)$ or $\varepsilon_x(V)$ in a practically accessible range of compressions and pressures are based on a quantum-mechanical consideration of interatomic interaction. In a number of cases it is then possible to obtain satisfactory agreement with experimental data on compressibility, in particular for alkali and alkali earth metals at small pressures. A detailed account of these calculations and a comparison with the experimental data of Bridgeman on static compression of substances to several tens of thousand atmospheres can be found in Gombash's book [13]; in the same place he gives literature references.

Detailed data on curves of cold compression of a number of metals (and also sodium chloride) up to pressures of several million atmospheres and densities, approximately two times greater than normal, were obtained by L. V. Al'tshuler, K. K. Krupnikov, S. B. Kormer, T. A. Bakanova, R. F. Trunin, M. N. Pavlovskiy, L. V. Kuleshova, and V. D. Urlin [1-5, 14, 15], on the basis of theoretical treatment of the results of experiments on shock compression.

The account of these experiments will go even further; here for illustration we will give curves $p_x(V)$ and $\varepsilon_x(V)$ for iron (Fig. 11.2).

Theoretically it is possible to establish a limiting law for cold compression of a substance at very large pressures and densities. Under condtiions of very strong compression electron shells of atoms in some measure lose their individual structure. The state of the substance in this case can be approximately described with the help of the statistical model of an atom of Thomas and Fermi, or, slightly more exact, with the help of the model of Thomas, Fermi, and Dirac (this one considers exchange energy.* The equation of state of a substance in the model of Thomas and Fermi was discussed in § 13 of Chapter III. In the limit of very large pressures and densities the pressure of cold compression is

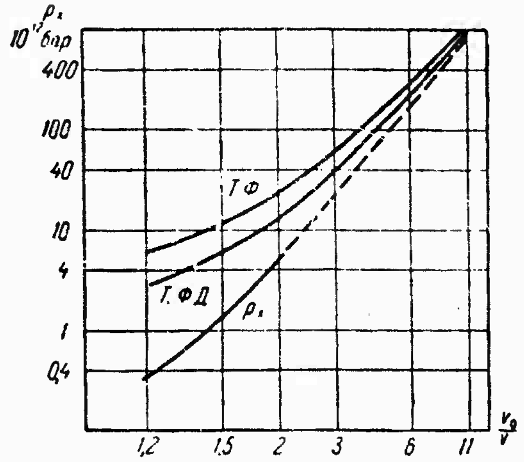

Fig. 11.3. Elastic pressure p_x of iron. p_x — experimental curve; T. F. — analytical curve of Thomas and Fermi; T. F. D. — Thomas, Fermi, and Dirac. Dotted line — extrapolation of p_x. Along the axis of abscissas compression V_0/V is plotted.

$$p_x \sim \varrho^{\frac{5}{3}} \sim V^{-\frac{5}{3}}. \qquad (11.3)$$

This law is also limiting for the most statistical model of an atom, since at not too large compressions the model leads to another dependence $p_x(V)$. In order to compare the actual curves of elastic pressure with the curves obtained in the statistical model, we shall present a graph from [1], which depicts in logarithmic scale the empirical curve for iron and curves calculated by the methods of Thomas and Fermi and Thomas, Fermi, and Dirac (Fig. 11.3).

From the figure it is clear that at compressions 1.2 to 1.8

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*Calculations by the Thomas, Fermi, and Dirac method have real meaning only in those cases when the exchange correction is shall. They essentially indicate the limits of applicability of the method of Thomas and Fermi. If the exchange correction turns out to be great, this means that the method of Thomas, Fermi, and Dirac no longer has force.

times, carried out by experiment, the statistical models give extremely oversized values of pressure. Quantum-mechanical calculations of the curve of cold compression of iron in a wide range of pressures were conducted by G. M. Gandel'man [37].

§ 3. Thermal Motion of Atoms

During heating the atoms of a substance are set into motion. Thermal motion of atoms is connected with defined energy and pressure. At temperature of the order of ten thousand degrees and higher an essential role is played by thermal excitation of electrons.

As was already noted in the preceding paragraph, total energy and pressure can be presented in the form of the sum of elastic and thermal components. In turn, the thermal members will be separated into two parts: terms corresponding to thermal motion of atoms (nuclei) — ε_t, p_t, and terms responding to thermal excitation of electrons — ε_e, p_e. Specific internal energy and pressure of a solid will then be written in the form

$$\varepsilon = \varepsilon_x + \varepsilon_T + \varepsilon_e, \qquad (11.4)$$

$$p = p_x + p_T + p_e. \qquad (11.5)$$

We shall take up the electron members later on. At temperatures approximately below ten thousand degrees the electron members are small and in expressions (11.4) and (11.5) it is possible to limit ourselves only to the first two terms.

Let us consider thermal motion of atoms. Here we will not make a distinction between a solid and a liquid and will not remain on the effect of melting. Thermal motion in a liquid hardly differs at all from thermal motion of atoms in a solid. Energetically, melting hardly shows up in the thermodynamic functions of a substance at high temperatures of the order of ten thousand degrees and above, since melting heat is comparatively small. For instance, in lead at normal pressure the melting point is $T_{melt} = 600^{o}K$, and melting heat is $U_{melt} = 1.3$ kcal/mole, which corresponds to $650^{o}K$ if we divide this magnitude by the gas constant R = 2 cal/mole•deg; in iron $T_{melt} = 1808^{o}K$, $U_{melt} = 3.86$ kcal/mole, and $U_{melt}/R = 1940^{o}K$.

If the temperature is not too high, the atoms of a solid (and liquid) accomplish small oscillations near the positions of equilibrium (nodes of the crystal lattice in a solid). The oscillations are harmonic as long as their amplitude is much less than the interatomic distance; in other words, until the energy of oscillations, which on the order of kT per atom, is considerably less than the height of the potential barrier for jumps of atoms from nodes of the lattice to the internodes or to other free nodes. At normal density of a solid the height of the barriers has the order of one or several electron volts,* i.e., the magnitude kT is compared with the height of the potential barrier at temperatures of the order of ten or several tens of thousand degrees. At higher temperatures the atoms can almost freely move along the body. Thermal motion then loses its oscillatory character and more quickly approaches a chaotic character, like a gas: the substance is turned into a dense gas from the strongly interacting atoms.

The situation changes however, if simultaneously with heating the substance is compressed. During compression the height of the

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*This is a magnitude equal approximately to the activation energy for self-diffusion of atoms in a body ΔU. It is usually somewhat less than binding energy, but of the same order as the latter, $\Delta U \approx (0.5\text{-}0.7)$ U.

potential barrier very sharply increases, which the atom must overcome in order to depart from its cell (from its node of the crystal lattice). Free movements of atoms in the body in this instance are strongly hampered and the motion of the atom remains limited to the space of its cell. This is explained in Fig. 11.4.

In some rough approximation the thermal motion of atoms in a compressed substance can be considered as small oscillations near equilibrium positions even at the maximum temperatures of 20,000-30,000°K, which are attained in the most powerful shock waves investigated in experiment.

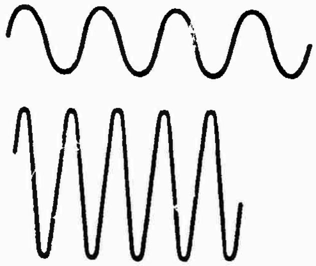

Fig. 11.4. Diagram explaining the change of height of potential barriers for atoms in a solid during compression.

At temperatures above several hundreds of degrees Kelvin the quantum effects in oscillations do not play a role, and the heat capacity of a body, whose atoms accomplish harmonic oscillations, is equal to its classical value of 3 k per 1 atom or $c_V = 3Nk$ per 1 g, where N is the number of atoms per gram. Taking into account the distinction of heat capacity from this value at low temperatures in a quantum region, we will write an expression for thermal energy, connected with oscillations of atoms, in the form

$$\varepsilon_T = c_V (T - T_0) + \varepsilon_0, \quad c_V = 3Nk, \qquad (11.6)$$

where $\varepsilon_0 = \int_0^{T_0} c_V(T)\,dT$ is the thermal energy at room temperature T_0, which can be taken from the appropriate table.

At temperatures T, considerably exceeding T_0, it is possible to disregard the distinction of $c_V T_0$ from ε_0, since both of these magnitudes are small as compared to $c_V T$. In this instance,

$$\varepsilon_T = c_V T, \quad c_V = 3Nk. \tag{11.7}$$

Heat capacity is equal to 3 k per atom only when the thermal motion of atoms has an oscillatory character. At sufficiently high temperatures the atoms freely move through the body; heat capacity corresponds only to forward degrees of freedom of atoms and is equal to $\frac{3}{2}$ k per atom, as in a monatomic gas. Transition from oscillatory motion of atoms to forward and the decrease of heat capacity connected with it occurs gradually in the region of such temperatures at which the kinetic energy of an atom $\frac{3}{2}$ kT on the order of the height of the potential barrier for movements of atoms in the body $\Delta U/N$. An effective boundary, separating the regions with limiting values of heat capacity 3 k and $\frac{3}{2}$ k, can be temperature:

$$T_k = \frac{2}{3}\frac{\Delta U}{kN}. \tag{11.8}$$

At high temperatures $T \gg T_k$ the thermal energy of one atom can be presented in the form of the sum of the kinetic energy of forward motion $\frac{3}{2}$ kT and the mean value of potential energy, which in the case of small oscillations also was equal to $\frac{3}{2}$ kT, and now is on the order of $\Delta U/k$.

This is in accordance with the effective determination of heat capacity by a discontinuous formula:

$$c_V = 3Nk \text{ when } T < T_k; \quad c_V = \frac{3}{2}Nk \text{ when } T > T_k.$$

If $T > T_k$, the energy is then equal to

$$\varepsilon_T = \int_0^T c_V\, dT = \int_0^{T_k} 3Nk\, dT + \int_{T_k}^T \frac{3}{2}Nk\, dT = \frac{3}{2}NkT + \Delta U. \tag{11.9}$$

For an example we will indicate that in iron of normal density

$$\frac{\Delta U}{k} \approx 2{,}5 \text{ ev and } T_k \approx 20\,000^\circ \text{K}.$$

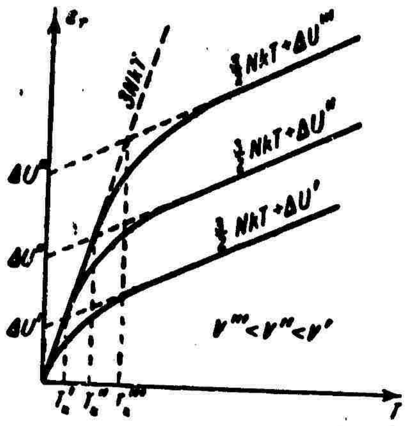

Fig. 11.5. Dependence of thermal energy on temperature at different densities (volumes).

During compression of a body the height of the potential barrier increases and threshold temperature T_k rises, so that curves of the dependence of thermal energy on temperature at various densities (volumes) have the form schematically depicted in Fig. 11.5.

In a limiting case $T \gg T_k$ when the thermal motion of atoms (more exact, nuclei) does not differ from gas motion, the thermal pressure connected with this motion is equal, as usual, to

$$p_T = nkT = \frac{NkT}{V} = \frac{2}{3}\frac{\varepsilon_T}{V}.$$

§ 4. Equation of State of a Body Whose Atoms Accomplish Small Oscillations

We shall consider that the atoms of a body accomplish small oscillations near equilibrium positions, and will find the magnitude of thermal pressure $p_T(V, T)$, responding to these oscillations. If temperature is not too high and electron excitation can be disregarded, the equation of state and internal energy of the body can then be written in the form

$$p = p_x(V) + p_T(V, T), \qquad (11.10)$$

$$\varepsilon = \varepsilon_x(V) + 3NkT. \qquad (11.11)$$

Temperature dependence of thermal pressure can be immediately established with the help of a general thermodynamic identity:

$$\left(\frac{\partial \varepsilon}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p. \qquad (11.12)$$

Elastic members, in accordance with equation (11.1), satisfy this relationship automatically. Noting that heat capacity $c_V = 3Nk$ does not depend on volume, we will obtain from formula (11.12) that thermal pressure is proportional to temperature: $p_T = \varphi(V)T$, where $\varphi(V)$ is a certain function of volume.

Let us rewrite this formula in the form

$$p_T = \Gamma(V)\frac{c_V T}{V} = \Gamma(V)\frac{\varepsilon_T}{V}. \tag{11.13}$$

Magnitude G, characterizing the ratio of thermal pressure to thermal lattice energy, is called the Grueneisen coefficient. The Grueneisen coefficient at normal volume of bodies $G_0 = G(V_0)$ is connected with the other parameters of the substance by a known thermodynamic relationship (see for instance [16]):

$$\left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_p \left(\frac{\partial V}{\partial p}\right)_T = -1. \tag{11.14}$$

Inasmuch as $\frac{1}{V_0}\left(\frac{\partial V}{\partial p}\right)_T = \varkappa_0$ is the isothermal compressibility of a substance at normal conditions, and $\frac{1}{V_0}\left(\frac{\partial V}{\partial T}\right)_p = \alpha$ is the coefficient of volume thermal expansion, we obtain

$$\Gamma_0 = \frac{V_0\alpha}{c_V\varkappa_0} = \frac{\alpha}{\rho_0 c_V \varkappa_0} = \frac{\alpha c_0^2}{c_V} \tag{11.15}$$

(c_0 is the speed of sound determined by compressibility).

The parameters of several metals at normal conditions are given in Table 11.1, taken from [3].*

The Grueneisen coefficient G corresponds to the adiabatic exponent decreased per unit in the case of an ideal gas with constant

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*The fact that β_0 is such will be discussed in the following paragraph.

heat capacity (let us recall the equation of state of a gas $p = (\gamma - 1)\,\frac{\varepsilon}{V}$).

Table 11.1. Certain Characteristics of Metals at Normal Conditions

	Al	Cu	Pb
ρ_0, g/cm^3	2.71	8.93	11.34
$c_V \cdot 10^{-6}$, erg/g·deg	8.96	3.82	1.29
$\varkappa_0 \cdot 10^{12}$, cm^2/d	1.37	0.73	2.42
$\alpha \cdot 10^5$, deg^{-1}	2.31	1.65	2.9
G_0	2.09	1.98	2.46
c_0, km/sec	5.2	3.95	1.91
$\varepsilon_0 \cdot 10^{-8}$, erg/g	16.1	7.71	3.23
β_0, erg/g·deg^2	500	110	144

By virtue of the condition adopted in the derivation of formula (11.13) that heat capacity c_V does not depend on volume, the Grueneisen coefficient turned out to be not depending on temperature. In reality, in the limit of very high temperatures, when thermal motion of atoms (nuclei) becomes chaotic, equation (11.13) should be turned into the equation of state of a monatomic gas, i.e., $G \rightarrow \frac{2}{3}$ when $T \rightarrow \infty$. If we imagine that the atoms of the body are disconnected and diverge at large distances by an external force (volume increases) the substance is turned into a gas even at low temperature, so that formally when $V \rightarrow \infty$, $G \rightarrow \frac{2}{3}$. As can be seen from the table, in normal conditions the Grueneisen coefficients of metals are close to two.

In order to clarify the physical meaning of the arbitrary function, i.e., the Grueneisen coefficient $G(V)$, which appeared formally as a result of integration of thermodynamic identity (11.12), one should turn to the expression known from statistical physics for free energy of a body whose atoms accomplish harmonic oscillations. At high temperatures, when kT is much greater than the energy of oscillatory quanta $h\nu$, the specific free energy is equal to (see [16])

$$F = \varepsilon_x(V) + 3NkT \ln \frac{h\bar{\nu}}{kT}, \qquad (11.16)$$

where $\bar{\nu}$ is a certain average frequency of oscillations, which is connected with Debye temperature θ by the relationship $h\bar{\nu} = e^{-1/3}k\theta = 0.715\, k\theta$ (for instance, in iron $\theta = 420^{\circ}K$). The first member in (11.16) constitutes the potential energy of interaction of atoms, coinciding with the energy of a cold body. The second member describes the thermal part of free energy. From formula (11.16) with the help of general thermodynamic relationships it is easy to find the specific internal energy and pressure of the body:

$$\varepsilon = F - T\frac{\partial F}{\partial T} = \varepsilon_x(V) + 3NkT = \varepsilon_x + \varepsilon_T$$

(we naturally arrived at formula (11.11)) and

$$p = -\frac{\partial F}{\partial V} = -\frac{d\varepsilon_x}{dV} - 3NkT\frac{\partial \ln \bar{\nu}}{\partial V}.$$

The first term gives the elastic pressure already known to us, and the second gives the thermal pressure. Taking into account the determination of the Grueneisen coefficient (11.13), we find

$$\Gamma(V) = -\frac{\partial \ln \bar{\nu}}{\partial \ln V}. \qquad (11.17)$$

The Grueneisen coefficient can be connected with the function of cold compression by means of the following simple reasoning. Average frequency of the spectrum of elastic lattice oscillations $\bar{\nu}$, is obviously close to maximum frequency. Maximum frequency in order of magnitude is equal to the ratio of speed of propagation of elastic waves of volume compression c_0 to minimum wave length, which in turn is on the order of the interatomic distance r_0, so that $\bar{\nu} \sim c_0/r_0$. But speed of sound $c_0 = \left(-V^2\frac{dp_x}{dV}\right)^{1/2}$, and $r_0 \sim V^{1/3}$, whence

$$\bar{\nu} \sim V^{\frac{2}{3}}\left(-\frac{dp_x}{dV}\right)^{\frac{1}{2}}.$$

Taking the logarithmic derivative from this expression, we obtain

$$\Gamma(V) = -\frac{\partial \ln \bar{\nu}}{\partial \ln V} = -\frac{2}{3} - \frac{V}{2}\left(\frac{d^2p_x}{dV^2}\right)\Big/\left(\frac{dp_x}{dV}\right). \qquad (11.18)$$

This formula was obtained by Slatter [17] and L. D. Landau and K. P. Stanyukovich [18].

Experience shows that Grueneisen coefficients decrease somewhat during compression (with decrease of specific volume V).

In order to imagine the order of magnitude of thermal pressure (11.13), we shall indicate that if, for instance, we heat aluminum at a constant volume equal to normal, to a temperature of 1000°K, the pressure in it drops to the magnitude $p_T = 51{,}000$ atm.

During heating of a solid in usual conditions, i.e., at constant atmospheric pressure, the body is expanded. The cause of thermal expansion of bodies is absolutely clear; one only has to glance at the formula for pressure (11.10). During heating the positive thermal pressure p_T increases. So that total pressure remains constant, elastic pressure p_x must become negative, i.e., the body must expand as long as there are adhesive forces holding the atoms in the lattice, or the negative pressure will not balance the repulsive action of positive thermal pressure. Hence, the relation becomes clear between the Grueneisen coefficients, thermal expansion, and compressibility, which is expressed by formula (11.15). Actually, small expansion at constant pressure is connected with small heating by the condition

$$dp = dp_x + dp_T \approx \frac{dp_x}{dV}\,dV + \frac{\partial p_T}{\partial T}\,dT = \frac{dp_x}{dV}\,dV + \Gamma_0 \frac{c_V}{V_0}\,dT = 0,$$

whereupon there follow the relationships (11.14) and (11.15).*

Let us estimate, for example, how much aluminum expands, if we heat it at constant pressure (zero or atmospheric, it makes no difference) from absolute zero to room temperature T = 300°K. Using the constants given in Table 1.1, we find $\Delta V/V \approx G_0 \frac{c_V}{V_0} \varkappa_0 \Delta T \approx$ $\approx 2\%$ $(\Delta T = 300^\circ\ \mathrm{K})$.

Moreover, in the state with $T_0 = 300^\circ$K the thermal pressure is the same as the absolute value of elastic pressure, equal to $p_{T0} = 17{,}000$ atm. Hence it is clear that atmospheric pressure can always be considered to be equal to zero, since it is insignificant in comparison with both components of pressure even at room temperature.

If we know function G(V), it is easy to find the entropy of the substance. Considering a state, slightly differing in density from normal, it is possible to consider G as constant and equal to its normal value of G_0. For entropy we then obtain the equation

$$dS = \frac{d\varepsilon + p\,dV}{T} = \frac{d\varepsilon_T + p_T\,dV}{T} = c_V \frac{dT}{T} + \Gamma_0 c_V \frac{dV}{V},$$

---

*We consider only a substance with normal properties, expanding during heating.

whence the specific entropy is equal to

$$S = c_V \ln \frac{T}{T_0}\left(\frac{V}{V_0}\right)^{\Gamma_0} + S_0, \qquad (11.19)$$

where S_0 is entropy at normal conditions T_0 and V_0, which can usually be found in tables. The adiabatic bond of temperature and volume is given by the equation

$$\frac{T}{T_0} = \left(\frac{V_0}{V}\right)^{\Gamma_0}{}^{*} \qquad (11.20)$$

Expressing temperature through pressure with the help of the equation of state

$$p = p_x(V) + \Gamma_0 \frac{c_V T}{V}, \qquad (11.21)$$

we find the adiabatic bond of pressure and volume:

$$\frac{p - p_x(V)}{p_{T_0}} = \left(\frac{V_0}{V}\right)^{\Gamma_0 + 1}, \qquad (11.22)$$

where $p_{TO} = G_0 c_V T_0/V_0$ is the thermal component of pressure at normal conditions.** In small compressions which nonetheless are accompanied by an abrupt increase of pressure (as compared to atmospheric, but not with p_{TO}), the adiabat p(V) spreads at an almost constant distance from the curve of cold compression $p_x(V)$.

During relatively large compressions (1.5-2 times) $p \gg p_{TO}$ and the relative deviation of the adiabat from the curve of cold compression $[p - p_x(V)]/p_x(V)$ becomes small.

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*Compare with the adiabatic bond of T and V in a gas with constant heat capacity $T \sim V^{-(\gamma-1)}$; G corresponds to $\gamma - 1$.

**The isotherm is $[p - p_x(V)]/p_{T_0} = V_0/V$. At small changes of volume the isotherm almost coincides with the adiabat (change of pressure is great).

§ 5. Thermal Excitation of Electrons

In the simplest models of metallic bodies the external valence electrons of atoms of the metal are torn from their places in the atoms and all together form a free electron gas, completely filling a crystal body, in the nodes of which there are ions or atomic remainders.* The electron gas follows the quantum statistics of Fermi and Dirac, the elements of which were presented in § 12 of Chapter III.

At absolute zero temperature the electron gas is completely degenerated; in accordance with the Pauli principle the electrons occupy the lowest energy states and possess kinetic energy not exceeding the end-point energy of Fermi (3.88):

$$E_0 = \frac{h^2}{8\pi^2 m_e} (3\pi^2 n_e)^{\frac{2}{3}}$$

(n_e is the number of free electrons per 1 cm^3, m_e is the mass of an electron).

Energy E_0 in metals usually has an order of several electron-volts, and the temperature of degeneration corresponding to it, $T^* = E_0/k$, is on the order of several tens of thousand degrees.**

Kinetic energy of the completely degenerated electron gas, which is on the order of E_0 per electron, is included in the elastic energy of the body and is not related to thermal energy. In exactly the same way, the "kinetic" pressure corresponding to it is included in elastic pressure along with the "potential" pressure

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*We shall limit ourselves here to elementary presentations, not concerning the contemporary electron theory of metals.

**For instance in Na, $T^* = 37,000^\circ K$, in K — $24,000^\circ K$, in Ag — $64,000^\circ K$, and in Cu — $82,000^\circ K$.

caused by the electrostatic interaction of electrons and ions. In summary, this total pressure of nonthermal origin is equal to zero, if the body is in a vacuum at absolute zero temperature.

With increase of temperature the electrons partially pass into higher energy states, exceeding Fermi end-point energy, and the energy of the electron gas is increased.

If temperature T is much less than Fermi temperature T*, then roughly speaking, from the initial Fermi sphere in the space of momentum there burst electrons, removed from the Fermi level at an energy distance of the order kT. The number of excited electrons is a fraction on the order of kT/E_0 of the total number of electrons. Each of them obtains additional energy of order kT. Thus, thermal energy per electron in order of magnitude is equal to $(kT/E_0)kT$ and is proportional to $V^{2/3}T^2$ (since $E_0 \sim n_e^{2/3} \sim V^{-2/3}$). Taking into account the numerical coefficient the thermal energy of electrons, calculated per g of metal when T << T*, turns out to be equal to (see for example [16])

$$\varepsilon_e = \frac{1}{2}\beta T^2, \tag{11.23}$$

where coefficient β depends on the density of the substance and is equal to

$$\beta = \beta_0\left(\frac{V}{V_0}\right)^{\frac{2}{3}}; \quad \beta_0 = \frac{4\pi^4}{(3\pi^2)^{\frac{2}{3}}}\frac{k^2 m_e}{h^2}N_e^{\frac{1}{3}}V_0^{\frac{2}{3}} \tag{11.24}$$

(N_e is the number of free electrons per g of metal; V_0 is the normal specific volume of the metal). Specific heat capacity at constant volume is proportional to temperature and is equal to

$$c_{V_e} = \beta T. \tag{11.25}$$

Knowing the number of free electrons per atom of metal, it is possible by formula (11.24) to calculate coefficient β_0 and find electron heat capacity at a given temperature. In an experiment the electron heat capacity is measured at very low temperatures, at which lattice heat capacity obeys quantum laws and is proportional to T^3. At sufficiently low temperatures electron heat capacity predominates, is proportional only to the first power of T, and it can be measured. At room temperature the electron heat capacity is usually tens and even one hundred times less than lattice heat capacity, which in these conditions is constant and is equal to its classical magnitude $c_V = 3Nk$.

Experimental values of coefficients of electron heat capacity β_0 for several metals are given in Table 11.1.*

If we compare the values of heat capacities of electrons and lattice at different temperatures, it is possible to see that already at a temperature of the order of 10,000°K the electron heat capacity becomes very noticeable, and, let us say, at 50,000°K it is even greater than lattice heat capacity. It should be considered, however, that dependence (11.25) is valid only as long as the temperature is less than Fermi temperature.

When $T \gg T^*$ the free electron gas with constant number of electrons is not degenerated, and its heat capacity is equal to the classic value of $c_{V_e} = \frac{3}{2} N_e k$. In reality, at high temperatures the actual number of "free" electrons increases, and the electron heat capacity of the substance is not described by simple formulas. The question about the electron heat capacity of a dense gas at high

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*They coincide in order of magnitude with those calculated with formula (11.24).

temperatures was discussed in detail in § 14 of Chapter III.

At temperatures of order of 10,000-20,000°K, which had been attained in experiments on shock compression of metals, we are still far from this situation, and heat capacity of electrons can be approximately considered to be proportional to temperature, as follows from formula (11.25). It is necessary to say that temperature of degeneration T* increases during compression of metal ($T^* \sim V^{-2/3}$), so that the temperature range in which the approximation of $\varepsilon_e \sim T^2$ and $c_{V_e} \sim T$ is valid, in a compressed substance is greater than at normal density.

According to the equation of state for a free electron gas (both degenerated and also nondegenerated), the thermal part of pressure of electrons is equal to

$$p_e = \frac{2}{3}\frac{\varepsilon_e}{V} = \frac{1}{3}\beta\frac{T^2}{V} \sim V^{\frac{1}{3}}T^2. \qquad (11.26)$$

If we determine the "coefficient of Grueneisen" for electrons G_e by a relationship analogous to (11.13),

$$p_e = \Gamma_e\frac{\varepsilon_e}{V}, \qquad (11.27)$$

for a free electron gas it will be equal to 2/3.

S. B. Kormer [3] conducted a detailed analysis of the thermal behavior of electrons on the basis of statistical models of an atomic cell according to Thomas and Fermi and Thomas, Fermi, and Dirac (see § 12 to § 14 of Chapter III). He took the approximate calculations of Gilvarry [19], who considered the thermal members as a correction with respect to the model of a cold atom by Thomas and Fermi, the calculations of Latter [20], which were discussed in § 14 of Chapter III, and experimental data. This analysis showed that up to temperatures of the order of 30,000-50,000°K the heat capacity of electrons, as also in the model of free electrons, is proportional to temperature; $c_{V_e} \sim T$, $\varepsilon_e \sim T^2$, where with the growth of density such regularity is kept to all higher temperatures.

Regarding, however, thermal pressure, the coefficient G_e turns out to be equal to 2/3 only in limiting cases of very high temperatures or very large densities, when the kinetic energy of electrons is much greater than Coulomb energy. In the region of temperatures and densities realized in the experiments on shock compression the magnitude G_e is somewhat less; it is equal approximately to 0.5-0.6. As a result it turned out that it is possible with a sufficient degree of accuracy to take G_e = const = 1/2.

In order to avoid contradiction in this case with thermodynamic identity (11.2), together with the change of coefficient G_e it is necessary to simultaneously change the exponent in the dependence of energy on volume connected with it; namely, instead of $\varepsilon_e \sim V^{2/3}T^2$ the dependence $\varepsilon_e \sim V^{1/2}T^2$ should be taken.*

Considering the coefficient of electron heat capacity at normal volume to be equal to its experimental value, it is possible according to S. B. Kormer to write approximately, when T < 30,000-50,000°K:

$$\varepsilon_e = \frac{1}{2}\beta T^2, \quad \beta = \beta_0\left(\frac{V}{V_0}\right)^{\frac{1}{2}}, \tag{11.28}$$

$$p_e = \frac{1}{2}\frac{\varepsilon_e}{V}. \tag{11.29}$$

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*It is easy to check that in the dependence $\varepsilon_e \sim V^k T^2$ and equation of state $p = G_e \varepsilon_e / V$ with G_e = const, the thermodynamic identity is satisfied only when $k = G_e$.

§ 6. Trinomial Equation of State

Let us briefly summarize the results of §§ 2-5. The specific internal energy and pressure of a solid or liquid may be presented in the form of the sums of three components which describe the elastic properties of a cold body, the thermal motion of atoms (nuclei), and thermal excitation of electrons. Considering not too high temperatures, no higher than several tens of thousand degrees (and large compressions), it is possible in order of approximation to consider that atoms accomplish small oscillations and that their heat capacity is equal to $c_V = 3Nk$. Electron members with such temperatures are described by approximate formulas (11.28) and (11.29). Thus, energy and pressure are equal to:

$$\left.\begin{aligned} &\varepsilon=\varepsilon_x(V)+\varepsilon_T+\varepsilon_e, \quad p=p_x(V)+p_T+p_e,\\ &\varepsilon_x(V)=\int\limits_V^{V_{0x}} p_x(V)\,dV,\\ &\varepsilon_T=3Nk(T-T_0)+\varepsilon_0,\\ &\varepsilon_e=\frac{1}{2}\beta_0\left(\frac{V}{V_0}\right)^{\frac{1}{2}}T^2,\\ &p_T=\Gamma(V)\frac{\varepsilon_T}{V}, \quad p_e=\frac{1}{2}\frac{\varepsilon_e}{V}. \end{aligned}\right\} \qquad (11.30)$$

where

T_0 is room temperature; ε_0 is the thermal energy of an atomic lattice at room temperature, which is taken from tables. The coefficient of electron heat capacity at normal volume β_0 is taken from experiments on the measurement of heat capacity at very low temperatures.

The Grueneisen coefficient G(V) is connected with the function $p_x(V)$ by differential relationship (11.18). There remains only one unknown magnitude, i.e., elastic pressure as a function of volume $p_x(V)$, which should be found experimentally.

2. Shock Adiabat

§ 7. Shock Adiabat of a Condensed Substance

The laws of preservation of flows of mass, momentum, and energy on the front of a shock wave (1.61)-(1.63) have an absolutely general value, irrelevant to the aggregate state of a substance through which a wave is spreading. Inasmuch as even in very weak shock waves pressures are measured in thousands of atmospheres, initial atmospheric pressure can always be disregarded, considering it to be equal to zero. Let us designate, as usual through D, the speed of propagation of a shock wave through undisturbed substance, and through u, the jump of mass speed in the front, equal to the speed of the substance behind the front (in a laboratory system of coordinates), if the substances rests in front of the front. Omitting index for magnitudes behind the front, we shall write the laws of conservation of mass and momentum in the form

$$\frac{V_0}{V}=\frac{D}{(D-u)}, \tag{11.31}$$

$$p=\frac{Du}{V_0}. \tag{11.32}$$

Excluding from these equations speed u, we obtain

$$p=\frac{D^2}{V_0}\left(1-\frac{V}{V_0}\right). \tag{11.33}$$

As the third, energy relationship, we shall take the equation of shock adiabat (1.71) with $p_0 = 0$:

$$\varepsilon-\varepsilon_0=\frac{1}{2}p(V_0-V). \tag{11.34}$$

Total energy, obtained by 1 g of substance as a result of shock compression $p(V_0 - V)$, is distributed equally between kinetic $u^2/2$ and internal $\varepsilon - \varepsilon_0$ energies (in the system of coordinates where the undisturbed substance rests). Change of internal energy in turn is composed of changes of elastic and thermal energy.

We shall consider at first a shock wave spreading through a body with zero temperature: $T_0 = 0$, $\varepsilon_0 = 0$, $V_0 = V_{0c}$. On a diagram of p and V (Fig. 11.6) we draw the adiabat of cold compression $p_x(V)$ and shock adiabat $p_H(V)$ which is naturally higher, since total pressure behind the front is composed of elastic and thermal pressure. The elastic energy ε_x obtained by the substance is numerically equal to the area of curvilinear triangle OBC, shaded horizontally $\left(\varepsilon_x = \int_V^{V_{0c}} p_x \, dV\right)$. Total internal energy ε, according to (11.34), is equal to the area of triangle OAC; the difference of areas, shaded vertically, also composes the thermal energy of the substance, which was subjected to shock compression.

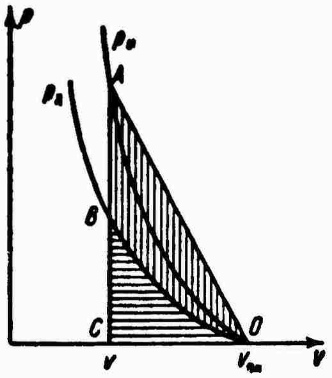

Fig. 11.6. p and V-diagram for shock compression of a cold substance. p_H — shock adiabat, p_x — curve of cold compression.

As can be seen from Fig. 11.6, the area of OAC is certainly greater than the area of OBC, only if the curve of cold compression is convex with respect to the axis of volumes $\left(\frac{d^2 p_x}{dV^2} > 0\right)$, which usually always occurs. Therefore, in the shock wave the substance is always heated and its entropy is increased. This absolutely general position, graphically demonstrated in Chapter I in the specific example of an ideal gas with constant heat capacity, with no less clarity in the case of a solid follows from the

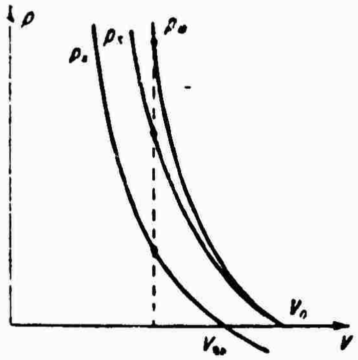

Fig. 11.7. p and V-diagram for shock compression of a solid body heated to room temperature. p_H — shock adiabat, p_S — isentrope, p_x — cold compression curve.

elastic properties of the substance.

We shall now consider shock compression of a body initially located at normal conditions V_0 and T_0. The initial elastic pressure in this instance is negative, and curve $p_x(V)$ is located as depicted in Fig. 11.7. The usual adiabat or isentrope $p_S(V, S_0)$, passing through the initial state, with decrease of volume deviates somewhat upwards from the curve of cold compression.

At small compressions the electron pressure is insignificantly small; the Grueneisen coefficient may be considered constant and adiabat $p_S(V, S_0)$ is described by equation (11.22).

As we know (Chapter I, § 18), the shock adiabat $p_H(V)$ at the initial point has a second order tangency with the usual adiabat $p_S(V)$, so that the shock adiabat proceeds as shown in Fig. 11.7. Figure 11.7 is carried out in such scales, in order to make graphic the mutual location of all three curves p_x, p_S, and p_H in a range of comparatively small pressures to a magnitude of the order of a hundred thousand atmospheres. If we consider a wide range of pressures to a million atmospheres, the distinction between V_0 and V_{0c}, the same as the deviation of the usual adiabat from the curve of cold compression, almost does not show up, and the deviation of shock adiabat from isentrope p_S or from curve p_x becomes considerable due to amplification of the role of the thermal components of energy and pressure, or the very same, due to a noticeable rise of entropy. The picture is then the same as in Fig. 11.6, where it is possible to consider $V_{0c} = V_0$ and adiabat p_{S_0} to be coinciding with the curve of cold compression.

In shock waves with pressures of the order of a million atmospheres, the thermal energy connected with the increase of entropy of the substance is comparable with total energy. In exactly the same way, the thermal pressure is comparable with total pressure. This is illustrated in Fig. 11.8, taken from [3], which represents experimental shock adiabats of copper and lead to pressures of the order of $4 \cdot 10^6$ atm and, obtained on the basis of experiments by means of calculation, curves of cold compression (along the axis of abscissas we do not plot volume, but magnitude of compression, $\frac{\rho}{\rho_0} = \frac{V_0}{V}$).*

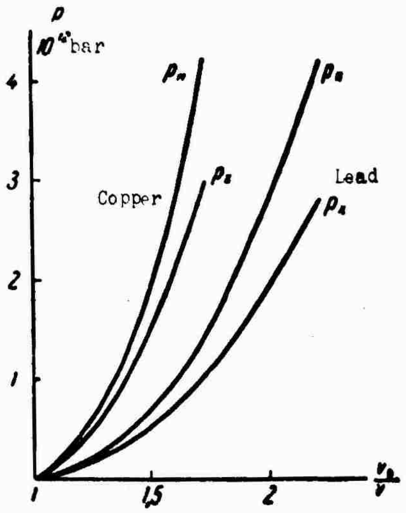

Fig. 11.8. Shock adiabats and curves of cold compression of copper and lead.

Considering Table 11.2, we can obtain a presentation about the relative role of all components of pressure and energy at different pressures of shock compression.**

Table 11.2. Parameters Behind the Front of a Shock Wave in Lead

$\frac{\rho}{\rho_0}$	p	p_x	p_T	p_e	$\varepsilon-\varepsilon_0$	ε_x	$c_V(T-T_0)$	ε_e	Γ	T, °K
	in 10^{10} d/cm² = 10^4 atm				in 10^6 erg/g					
1,3	25,0	21,6	3,35	0,051	25,4	15,3	9,6	0,69	1,9	1045
1,5	65,5	51,0	13,9	0,63	96,3	46,7	42,3	7,4	1,77	3580
1,7	133,0	95,3	34,0	3,8	242,0	95,8	107,0	39,4	1,60	8600
1,9	225,5	156,0	56,0	12,7	471,0	163,2	191,0	118,0	1,35	15100
2,1	335,5	233,0	73,0	29,0	775,0	248,0	284,0	243,0	1,07	22300
2,2	401,0	277,0	93,0	41,5	965,0	297,0	337,0	332,0	0,98	26400

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[*] These experiments and the method of obtaining the experimental curve of cold compressibility can be seen in §§ 12 and 13.

[**] The table is taken from [3]. To complete the picture we have added certain magnitudes to it. These magnitudes were calculated with the help of the constants given in [3].

From table it follows that during the shock compression of lead 2.2 times, the substance behind the front is heated to a temperature of 26,000°K; in this instance the thermal pressure composes 32% of the total, and thermal energy is 69% of the total, where half of the thermal energy belongs to the electrons, and half to the oscillations of atoms. Thermal pressure of electrons composes 34% of total thermal pressure.

In the qualitative aspect the behavior of all other investigated metals, upon increase of wave amplitude, was equal. Quantitative data can be found in [3]; we will not give them here.

The greater the amplitude of a shock wave, even greater will be the role played by the thermal components of pressure and energy. At very high pressures of the order of hundreds of million atmospheres and higher, the role of "elastic" components becomes small and the substance behaves practically as an ideal gas (ideal in the sense of the absence of interaction between particles). Correspondingly, the shock adiabat in these conditions in principle does not differ from the shock adiabat of an ideal gas (taking into account the processes of "ionization"; see Chapter III), i.e., and for a solid there exists a limiting compression in the shock wave. In the limit $p = \infty$ the temperature also tends to infinity, the atoms are completely ionized, and the substance is turned into an ideal, classic electron-nuclear gas with adiabatic exponent $\gamma = 5/3$, which corresponds to limiting compression equal to 4 (if we disregard the effects connected with radiation; see Chapter III).

§ 8. Analytic Presentations of Shock Adiabat

With the help of thermodynamic functions p(V, T) and ε(T, V) in principle we can find in evident form the equation of shock adiabat $p_H(V, V_0)$. Actually this is impossible to do, since the theoretical dependence of elastic pressure on volume is unknown, i.e., the function $p_x(V)$. It is useful, however, to write the equation of shock adiabat, leaving in it the unknown function $p_x(V)$. We shall consider shock waves of not too great amplitude, in which it is possible to disregard the electron components of pressure and energy and consider the Grueneisen coefficient G to be constant and equal to its value at normal conditions G_0.

At the same time we shall consider that the wave is not too weak, so that it is possible to disregard the initial energy of undisturbed substance ε_0. Actually this corresponds to the fact that we consider initial temperature to be equal to zero and do not make a distinction between normal volume V_0 and zero volume V_{0c}.

Let us place in the equation of shock adiabat (11.34) energy $\varepsilon = \varepsilon_x + \varepsilon_T$, expressing its thermal part ε_T through pressure by formula (11.21):

$$p - p_x = p_T = \Gamma_0 \frac{\varepsilon_T}{V}; \quad \varepsilon = \varepsilon_x + \frac{V(p - p_x)}{\Gamma_0}.$$

Solving the obtained equation with respect to p, we find the equation of shock adiabat in the form

$$p_H = \frac{(h-1)\,p_x(V) - 2\varepsilon_x(V)/V}{h - V_0/V}, \quad \varepsilon_x = \int_V^{V_{0x}} p_x(V)\,dV, \qquad (11.35)$$

where h designates the magnitude $h = 2/G_0 + 1$.

If we formally extend formula (11.35) to shock waves of very great amplitude, we will obtain that in the limit $p_H \to \infty$, $V_0/V = h$, i.e., h formally constitutes "limiting compression" in the shock wave. The position here is fully analogous to what takes place in an ideal gas with constant heat capacity. Let us remember that the index of Grueneisen G corresponds to the adiabatic exponent γ decreased by one. Hence "limiting compression" h corresponds to magnitude $(\gamma + 1)/(\gamma - 1)$, i.e., limiting compression for gases.

The formal analogy with gases is connected with the fact that in the limit $p_H \to \infty$ the thermal pressure plays a basic role ($p_T = p_H - p_x \to \infty$, when $p_x(V) \to \text{const}$) and the equation of state in this case does not differ from that of a gas.

Sometimes it is convenient to present shock adiabat in analytic form, using some interpolation formula. Experience shows that in a wide range of amplitudes of shock waves the dependence between speed of front and speed of substances behind the front (with respect to undisturbed) is linear:

$$D = A + Bu. \tag{11.36}$$

Thus, for instance, for iron A = 3.8 km/sec, B = 1.58).[*] With the help of relationship (11.36) by formula (11.34) and (11.32) it is easy to find the equation of shock adiabat:

$$p_H = \frac{A^2 (V_0 - V)}{(B-1)^2 V^2 \left[\frac{B}{B-1} - \frac{V_0}{V}\right]^2}. \tag{11.37}$$

Shock adiabat $p_H(V, V_0)$ can be interpolated by polynomials of the type

$$p_H = \sum_{k=1}^{m} a_k \left(\frac{V_0}{V} - 1\right)^k,$$

---

[*] Formula (11.36) cannot be extrapolated to small amplitudes $p \to 0$, $u \to 0$, so that constant A is not the speed of sound in a normal state.

by determining the constant coefficients partially from the results of experiments on shock compression, and partially through the parameters of the substance in normal state.

§ 9. Shock Waves of Weak Intensity

A region of pressures of the order of several tens and hundreds of thousand atmospheres has a large value for practice. These are the typical pressures which are developed in the detonation of explosives, in explosions in water, upon impact of detonation products against metal barriers, etc. In the region of isentropic flow we frequently use an empirical equation of state of a condensed substance of the type

$$p = A(S)\left[\left(\frac{V_0}{V}\right)^n - 1\right], \qquad (11.38)$$

in which index n is considered to be constant, and coefficient A depends on entropy; actually it is also always considered constant. Constants A and n are connected together by a relationship which includes compressibility of the substance at normal conditions (speed of sound)

$$c_0^2 = -V_0^2\left(\frac{\partial p}{\partial V}\right)_S = V_0 A n. \qquad (11.39)$$

F. A. Baum, K. P. Stanyukovich, and B. I. Shekhter [21], in accordance with Jensen's data, took for metals index n equal to 4 and calculated by formula (11.39) constants A for a number of metals through the experimental values of compressibility.

In a number of cases there was obtained good coincidence with values of A, which were determined by the same authors experimentally Thus, for instance, for iron $A_{cal} = 5 \cdot 10^5$ atm, which is 11% greater than experimental. For copper $A_{cal} = 2.5 \cdot 10^5$ atm, which is 6% greater than experimental; for duralumin $A_{cal} = 2.03 \cdot 10^5$ atm and practically coincides with the experimental value. For water we usually take $n \approx 7$-8 and $A \approx 3000$ atm.

During calculations of flows with shock waves in the region of shown pressures it is possible in the first approximation to disregard the change of entropy in the shock wave and to use the adiabatic equation of state (11.38) with A = const for the bond of pressure and compression in the front of the wave. With this speed D and u are found from the first two relationships on the front of the shock wave (11.31) and (11.32), or (11.31) and (11.33). Energy equation (11.34) can then be used so that in the following approximation we may estimate the increase of internal energy connected with the irreversibility of shock compression. Actually, if we consider (11.38) as an isentrope equation, the internal energy depending upon V can be found by using the equation $TdS = d\varepsilon + pdV = 0$:

$$\varepsilon(V) - \varepsilon_0 = -\int_{V_0}^{V} p\,dV = AV_0\left\{\frac{1}{n-1}\left[\left(\frac{V_0}{V}\right)^{n-1} - 1\right] - \left[1 - \frac{V}{V_0}\right]\right\}.$$

Equation of energy (11.34) on the front of a shock wave with this value of energy and the value of pressure according to (11.38) naturally is not satisfied. The difference

$$\Delta\varepsilon = \frac{1}{2}p(V_0 - V) - \int_{V}^{V_0}(p\ dV)_{S=\text{const}},$$

by definition is equal to the increase of internal energy connected with the growth of entropy in the shock wave. The smallness of this magnitude as compared to full increase of energy in the shock wave $\varepsilon - \varepsilon_0$ is also a condition of validity of the approximation of "adiabaticness" of shock compression.

Calculation of the ratio $\Delta\varepsilon/(\varepsilon - \varepsilon_0)$ with index $n = 4$ shows that when $V_0/V = 1.1$ this ratio is equal to 4.5%, and when $V_0/V = 1.2$ it is equal to 17.5% (ratio does not depend on A). Compression 1.1 times corresponds to pressures of order of 100,000 atm (for aluminum — 90,000 atm, for iron — 210,000 atm). Thus, at pressures of $\sim 10^5$ atm the approximation of "adiabaticness" of shock compression gives an error of no more than 5% with respect to energy (even less with respect to pressure), which permits us to consider the shock wave as acoustic in many practical calculations.

§ 10. Shock Compression of a Porous Substance

Unique peculiarities are possessed by the process of shock compression of porous bodies. Experimental study of shock compression of the same substance at different initial densities permits the obtainment of considerably more complete information about the thermodynamic properties of a substance at high pressures and temperatures. Porous bodies can have the most diverse nature and structure (powders, bodies with internal vacuums, fibrous bodies, etc.). All of them are characterized by the presence of more or less big particles or sections of solid substance with normal density $\rho_0 = 1/V_0$ and empty sections, owing to which the average specific volume V_{00} is greater than normal V_0 (and average density ρ_{00} is less than normal ρ_0). Let us imagine that a porous body is subjected to slow compression from all sides. At first the work of forces of external pressure is expended only for "closing" the vacuums, for sealing the substance, and reducing of it to normal volume. This work is connected with surmounting the forces of friction between particles, with breaking of particles, with crumpling of fibers, etc.

For accomplishment of this work there are required comparatively small pressures, the scale of which is the ultimate strength of materials, i.e., for metals, pressures of the order of a thousand atmospheres, and for many substances much smaller. If we considered compression in a range of pressures measured in hundreds of thousand atmospheres, then practically in that section of the adiabat where there occurs sealing of the substance to normal volume, pressure may be considered to be equal to zero, and adiabat passing from point V_{00} can be presented in the form of a segment of the axis of abscissas from V_{00} to V_0 ($p = 0$), and then during compression above normal density, in the form of an isentrope of solid substance (Fig. 11.9).

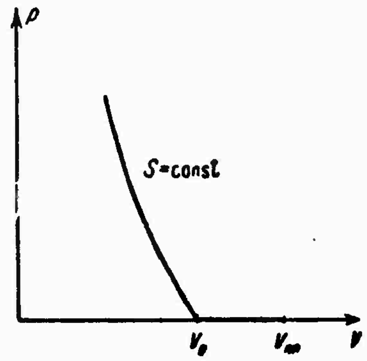

Fig. 11.9. Isentrope of compression of a porous substance.

We shall now consider shock compression of a porous body. For simplicity let us consider shock compression to high pressures measured in hundreds of thousand and million atmospheres, so that the usual adiabat of solid substance may be considered as coinciding with the curve of cold compression. Here we shall disregard the effects connected with strength and the distinction of initial temperature $T_0 \approx 300°$ from zero.

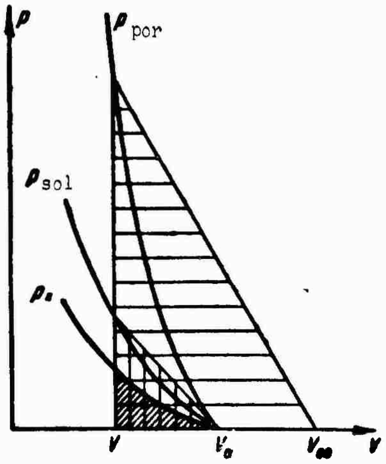

Fig. 11.10. p and V-diagram for shock compression of a porous substance. p_{por} — shock adiabat of a porous body, p_{sol} — shock adiabat of a solid body, p_x — curve of cold compression of a solid body.

We shall consider that in the final state behind the front of a shock wave the substance is solid and uniform. From the laws of preservation on the front of the shock wave and the equation of state of the substance it follows that the shock adiabat has the form depicted in Fig. 11.10 (this will be clarified below). The point corresponding to normal volume V_0 and zero pressure $p = 0$ lies on the shock adiabat. The internal energy obtained by the substance in the shock wave $\varepsilon = (1/2)p\ (V_{00} - V)$, is equal to the area of the triangle shaded horizontally. Its elastic part is equal to the area of the curvilinear triangle limited by curve $p_x(V)$ and covered in Fig. 11.10 by thick shading. The greater the initial volume V_{00}, i.e., the higher the porosity of the substance, the bigger the initial difference in areas, responding to part of the energy during compression of a porous substance to the same final volume (elastic energy at the given volume remains constant, and total energy grows).

But the greater the thermal energy, the higher the thermal pressure. Therefore, the higher the porosity, the higher the shock adiabat. In particular, the shock adiabat of a porous substance passes above the shock adiabat of a solid, as shown in Fig. 11.10.

In order to compress a porous substance to the very same volume as the solid, higher pressures are needed, whereby all the higher, the higher the degree of porosity.

The picture does not change in a qualitative aspect, if we consider initial temperature (and entropy) to be different from zero.

In order to obtain a presentation about how sharply the thermal components of pressure and energy increase during shock compression of a porous body as compared to compression of a solid, we will give

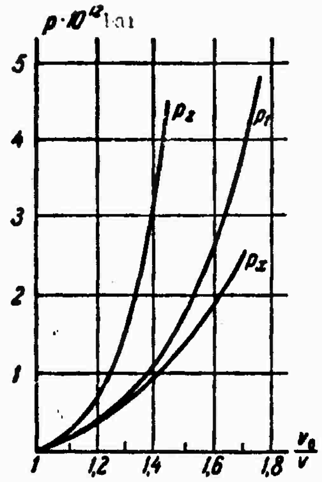

Fig. 11.11. Shock adiabats of solid (p_1) and porous (p_2) of iron. p_x — curve of cold compression.

experimental curves of shock adiabats of iron with normal density and porous iron with density lowered 1.4 times ($V_{00} = 1.412\ V_0$). These curves (Fig. 11.11) were taken from [1] (on the axis of abscissas we do not plot volume, but compression with respect to normal density V_0/V). For instance, during compression with respect to normal volume $V_0/V = 1.22$, which corresponds to a decrease of volume of porous iron by 1.74 times ($V_{00}/V = 1.74$); pressure in the case of porous iron turns out to be 2.63 times more than pressure for solid iron, and energy, in 8.64 times more.

Large heating during shock compression of porous bodies can lead to sharp anomalies in the trend of the shock adiabat. Namely, upon compression to a given pressure of a substance with high porosity, the relative role of thermal pressure turns out to be so great that the density in the final state at high pressure turns out to be less than normal ($V > V_0$). The volume with the growth of pressure does not decrease in this case, as usual, but increases, and the shock adiabat has the anomalous behavior depicted in Fig. 11.12.

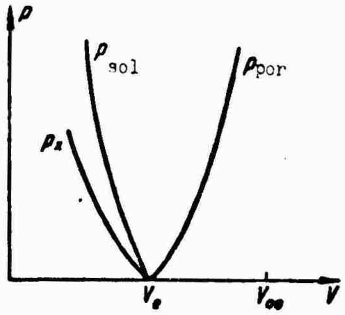

Fig. 11.12. Anomalous behavior of shock adiabat at high porosity of a substance.

In order to explain the origin of this curious effect, we will use the equation of shock adiabat concluded on the assumption that electron pressure and energy is low the Grueneisen coefficient is constant, and initial energy of the substance can be disregarded.

This is equation (11.35), in which under initial volume V_0 we understand the initial volume of a porous substance V_{00} (in the derivation of equation (11.35) nowhere is it mentioned that the substance in initial state is solid):

$$p_H(V, V_{00}) = \frac{(h-1)\,p_x(V) - \frac{2\varepsilon_x(V)}{V}}{h - \frac{V_{00}}{V}}, \quad h = \frac{2}{\Gamma_0} + 1. \qquad (11.40)$$

Equation (11.40) describes a family of shock adiabats corresponding to different initial volumes V_{00}, i.e., different degrees of porosity, which can be characterized by the coefficient $k = V_{00}/V_0 \geq 1$. When $k = 1$ and $V_{00} = V_0$ we have the shock adiabat of a solid substance. Point $V = V_0$ and $p_H = 0$ satisfies equation (11.40) at any initial volume V_{00} (since $p_x(V_0) = 0$, $\varepsilon_x(V_0) = 0$), so that the family of adiabats is a cluster of curves originating from this point. By formula (11.40) when $V_{00}/V \to h$, $p_H \to \infty$, i.e., limiting volume is $V_{lim} = V_{00}/h$. If this magnitude is less than V_0, $V_{lim} = V_{00}/h < V_0$, which takes place at small porosity $k < h$, the shock adiabats have a normal trend, whereby they are higher, the greater the initial volume. If, however, $V_{lim} > V_0$ (which occurs at high porosity, when $k > h$), the trend of the curves is anomalous: upon growth of pressure the final volume increases. The family of shock adiabats, corresponding to different coefficients of porosity, is shown in Fig. 11.13.

Let us emphasize once again that equation (11.40) describes only the initial trend of shock adiabats, in the region of small pressures. In reality, at large pressures the role of the electron members is essential, and the Grueneisen coefficient is not constant. But this does not disturb the validity of the qualitative conclusion concerning the possibility of anomalous behavior of the shock adiabat of an extremely porous substance.

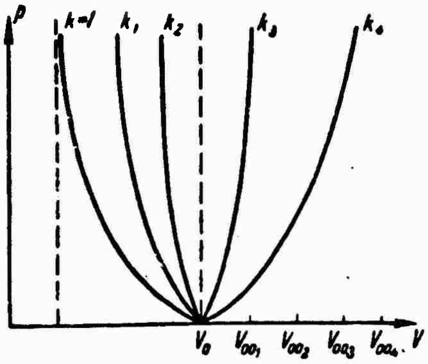

Fig. 11.13. Shock adiabats at different degrees of porosity: $k_4 > k_3 > h$; $h > k_2 > k_1 > 1$.

§ 11. Emergence of a not Very Strong Shock Wave on the Free Surface of a Body

In the experimental determination of shock adiabat of a solid, which will be considered in the following paragraph, we have widely used the so-called rule of doubling of speeds in an unloading wave.

When a shock wave, spreading through a solid, emerges on the free surface, the compressed substance is expanded, or, so to speak, is unloaded practically to zero pressure. The unloading wave (rarefaction wave) runs back through the substance with the speed of sound, corresponding to the state behind the front of a shock wave, and the unloaded substance itself obtains additional speed in the direction of the initial motion of the shock wave.*

In this paragraph we will consider only not very strong shock waves, which impart to the solid matter an energy insufficient for its melting, and all the more so for evaporation,** so that the final

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*If the body does not border with a vacuum, but with air, the moving boundary of the unloaded substance plays, with respect to the air, the role of a piston and "pushes" the air shock wave before it. Therefore, strictly speaking, the substance is unloaded not to zero pressure, but to the pressure in the air shock wave. However this pressure, which as compared to atmospheric can be larger, is so small as compared to the initial pressure in the solid compressed by the shock wave, that it can always be disregarded, and one may consider that unloading in air does not differ from unloading in a vacuum. The amplitude of a shock wave in air is then determined by the speed of the "piston," i.e., the speed of the unloaded solid matter.

**The evaporation of a solid that is initially compressed by a powerful shock wave will be discussed in §§ 21 and 22.

state of the substance after unloading will be assumed to be solid. The final volume of the unloaded substance V_1 in this case hardly differs from the normal volume of a solid V_0.

At the same time we will consider a shock wave that is not too weak, in such a manner so that it would be possible to disregard the effects connected with the strength of the solid. The pressure in a body compressed by a shock wave is assumed to be isotropic, as in a gas or liquid. This is valid when the pressure is great as compared to ultimate strength, critical shift stress, etc. Speed of sound is then determined by the compressibility of the substance and the modulus of total compression, exactly as in a gas and liquid. Otherwise unloading is described by formulas of the theory of elasticity, which will be discussed subsequently.

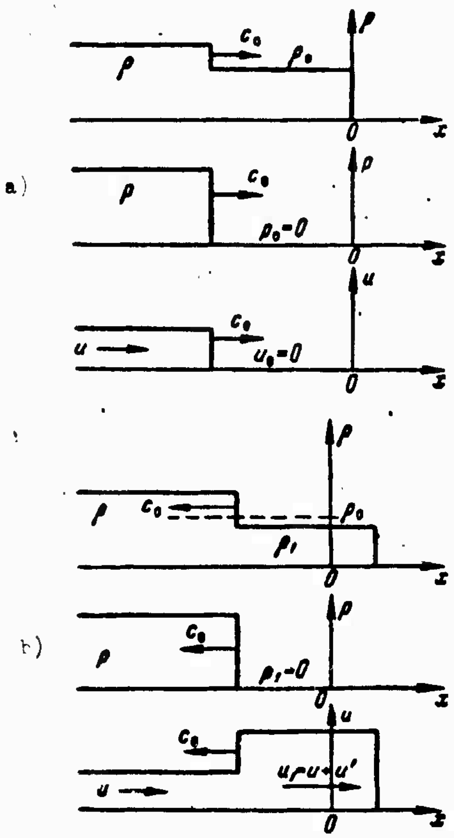

Fig. 11.14. Profiles of density, pressure, and speed at emergence of a weak shock wave on a free surface. a) before moment of emergence $t < 0$; b) after moment of emergence $t > 0$.

Let us assume that through the solid there spreads a plane shock wave of constant amplitude (pressure p, mass speed u, volume V, which is only somewhat less than normal volume V_0). In a defined moment of time the wave emerges on the free surface, which is considered the surface of the front of the shock wave. A not too strong shock wave, in which compression is small, $V_0 - V \ll V_0$, does not differ from an acoustic compressional wave and is described by formulas of acoustics. It spreads through the body with the speed of sound c_0. The pressure in it is connected with the mass speed by the relationship $p = \rho_0 c_0 u$ ($\rho_0 = 1/V_0$). Starting from moment $t = 0$ the emergence of the shock wave on the free surface, through the body there spreads an unloading wave backwards, which is also acoustic. It runs through the substance with the speed of sound (scarcely differing from the speed of sound in normal conditions c_0). Pressure in the wave drops from initial p to zero, and substance obtains speed u', connected with change of pressure $\Delta p = -p$ by the acoustic formula $u' = -\frac{\Delta p}{\rho_0 c_0} = \frac{p}{\rho_0 c_0}$ (Fig. 11.14; density decreases somewhat: final density ρ_1 scarcely differs from normal density of a solid: $V_1 - V_0 \ll V_0$). From comparison of formulas $p = \rho_0 c_0 u$ and $u' = p/\rho_0 c_0$, it is clear that the additional speed obtained by the substance during unloading u', is equal to the mass speed in the shock wave u, i.e., upon emergence of a not too strong shock wave on the free surface the speed of the substance doubles: $u' = u + u' \approx 2u$.

The rule of doubling of speeds can be also obtained from general equations for a shock wave and a wave of rarefaction, if we turn in them to the limiting case of small amplitudes of waves.

From gas dynamics we know (see § 10, Chapter I) that the additional speed obtained by a substance during unloading, from initial pressure p to final $p_1 = 0$, is equal to:

$$u' = \int_0^p \frac{dp}{\rho c} = \int_0^p \left(-\frac{\partial V}{\partial p}\right)_S^{\frac{1}{2}} dp = \int_V^{V_1} \left(-\frac{\partial p}{\partial V}\right)_S^{\frac{1}{2}} dV,$$

where the derivatives by virtue of the adiabaticness of the process of unloading are taken at constant entropy equal to entropy in the front of a shock wave. Initial mass speed of the substance in a shock wave by virtue of the laws of preservation (11.31) and (11.32) is equal to:

$$u = \sqrt{p(V_0 - V)}.$$

In a shock wave of small amplitude, where the change of entropy is small, the compression is also small; in the first approximation the increase of volume can be presented in the form

$$V - V_0 = \left(\frac{\partial V}{\partial p}\right)_S p,$$

implying by S the entropy of the initial state of the substance until compression by the shock wave. Then mass speed in the shock wave is equal to

$$u \approx \left(-\frac{\partial V}{\partial p}\right)_S^{\frac{1}{2}} p \approx \frac{p}{\rho_0 c_0}.$$

In that same approximation it is possible to disregard the change of adiabatic compressibility in the range of pressures from 0 to p and in the formula for u' to consider the derivative as constant. We obtain

$$u' = \int_0^p \left(-\frac{\partial V}{\partial p}\right)_S^{\frac{1}{2}} dp \approx \left(-\frac{\partial V}{\partial p}\right)_S^{\frac{1}{2}} p \approx \frac{p}{\rho_0 c_0} \approx u.$$

Walsh and Christian [22], from very general considerations, established the upper and lower limits for possible variations of the magnitude of additional speed u' and found that at pressures $p \sim 4 \cdot 10^5$ atm for a large number of metals the rule of doubling of speeds is valid with an accuracy of 2%. As an experimental check showed, conducted by the authors of [3], the rule of doubling of speeds for iron is executed approximately up to very high pressures $\sim 1.5 \cdot 10^6$ atm. In general, deviation from the rule of doubling of speeds is greater, the higher the amplitude of the shock wave.

We shall now take into account that a shock wave, even a weak one, is not acoustic, and the entropy in it is increased. Moreover, in first approximation, as before, we shall consider that the

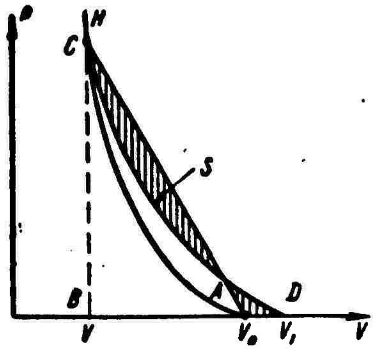

Fig. 11.15. p and V-diagram for shock compression and unloading of a solid.

additional speed after unloading u' is equal to u, and density and temperature in final state will be considered in the following approximation.

During adiabatic unloading of a body to initial, zero pressure, it turns out to be heated and expanded as compared to the initial state, until compression by the shock wave. It is easy to find the energy of irreversible heating and final temperature of an unloaded substance T_1, if we know the thermodynamic functions and initial state in the shock wave. For this we must use the equation of unloading adiabat $d\varepsilon + pdV = 0$, according to which the final energy ε_1 is equal to:

$$\varepsilon_1 = \varepsilon - \int_V^{V_1} (pdV)_S. \qquad (11.41)$$

Inasmuch as the energy in a shock wave is $\varepsilon = \varepsilon_0 + \frac{1}{2} p (V_0 - V)$, the irreversible increase of energy after unloading is equal to:

$$\varepsilon_1 - \varepsilon_0 = \frac{1}{2} p (V_0 - V) - \int_V^{V_1} (pdV)_S. \qquad (11.42)$$

The magnitude of this energy is depicted by the difference of areas of curvilinear triangle DBCS and triangle ABC in Fig. 11.15, in which curve H constitutes the shock adiabat, and curve S is the adiabat of unloading. Numerically this energy is equal to the difference of areas of the upper and lower shaded figures.

We shall assume that the amplitude of the shock wave is small, so that all three volumes V, V_0, and V_1 hardly differ from each other and the coefficient of Grueneisen may be considered constant and equal to its normal value G_0. In this case the adiabatic bond of temperature and volume is given by formula (11.20), so that final temperature T_1 is connected with the temperature in the shock wave T by the relationship

$$\frac{T_1}{T} = \left(\frac{V}{V_1}\right)^{\Gamma_0}. \qquad (11.43)$$

On the other hand, considering the process of thermal expansion of a body at constant, zero pressure from initial volume V_0 to volume V_1, we can write

$$V_1 - V_0 = V_0 \alpha (T_1 - T_0), \qquad (11.44)$$

where α is the coefficient of volume thermal expansion. Irreversible increase of energy (11.42) is expressed through the increase of temperature by the formula

$$\varepsilon_1 - \varepsilon_0 = c_p (T_1 - T_0),$$

where c_p is heat capacity of a body at constant pressure.*

If we know the volume and temperature in a shock wave V and T, from the system of two equations (11.43) and (11.44) it is possible to calculate volume and temperature in final state.

As an example we shall give the results for aluminum, obtained in [23]. During shock compression of aluminum to pressure $p = 2.5 \cdot 10^5$ atm the volume decreased to the magnitude $V = 0.82\ V_0$, and temperature increased to $T - T_0 = 331^\circ K$ (initial temperature T_0 was equal to $300^\circ K$). After unloading the residual heating

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*In solids in a small range of changes of temperature it practically does not differ from heat capacity at constant volume c_V.

composed $T_1 - T_0 = 134^\circ K$.*

When $p = 3.5 \cdot 10^5$ atm, $V = 0.78\ V_0$, $T - T_0 = 522^\circ K$ and $T_1 - T_0 = 216^\circ K$.

Naturally, the stronger the wave, the greater the entropy it imparts to the substance and the higher the residual heating.

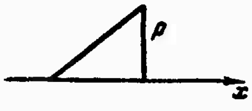

Fig. 11.16. Compression pulse of triangular form.

If through a flat plate there spreads a shock wave, behind the front of which the pressure and speed are not constant, and there is a drop, for instance, of compression pulse of triangular from (Fig. 11.16), after the emergence of such a wave on the free surface of the body there can occur break-away. The phenomenon of break-away consists in the following. After reflection of a compressional wave from the free surface the profile of pressure in the body will form as a result of the combination of two waves: incident — compressional waves, and reflected — unloading waves. In the acoustic approximation (see § 3 of Chapter I)

$$p=\rho c[f_1(x-ct)+f_2(x+ct)],$$

where function f_1 describes the incident wave which spreads with the speed of sound to the right, and f_2 is the reflected wave which spreads to the left. In this case the function f_1 corresponds to the triangular profile of pressure shown in Fig. 11.16. Function f_2 can be established by proceeding from the boundary condition, i.e., the equality to zero of pressure on the free surface.

Functions f_1 and f_2, and also the distributions of pressure

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*Residual temperature in [23] was calculated more exactly than given by formula (11.43), taking into account the small change of the Grueneisen coefficient during change of volume; for this we integrated the "exact" equation of adiabat with variable G(V).

composed from them, in the body at the time of emergence of the shock wave on the free surface and in two subsequent moments of time, are depicted in Fig. 11.17. If the coordinate of free surface is x_1 (Fig. 11.17), the region $x > x_1$ is empty and determination of functions f_1 and f_2 in region $x > x_1$ is purely formal. Physically, the real values are only the values of f_1 and f_2, and pressures when $x < x_1$, i.e., in the body. In order to emphasize this circumstance, functions f_1 and f_2 when $x > x_1$ in Fig. 11.17 are shown by the dotted line.

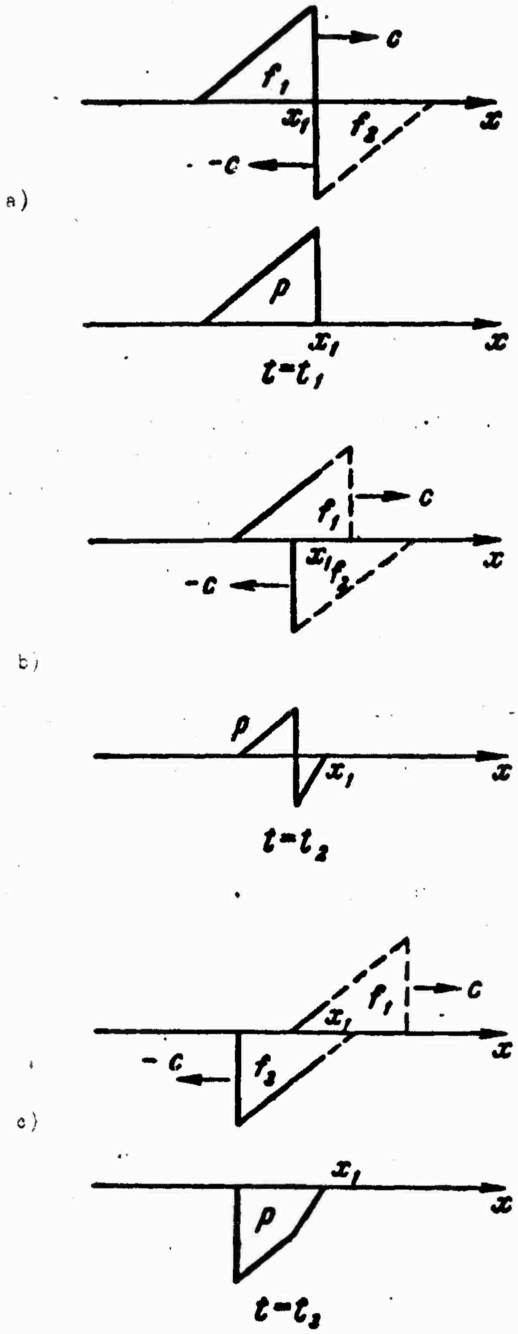

Fig. 11.17. Reflection of an acoustic compressional wave of triangular profile from a free surface. a) $t = t_1$ pertains to the moment of emergence of the leading front of the wave on the free surface; b) $t = t_2$, and c) $t = t_3$ pertains to subsequent moments.

From Fig. 11.17 it is clear that after reflection of a compressional wave from the free surface in the body there appear negative pressures, i.e., the body experiences a tensile force. If tensile stress exceeds ultimate tensile strength of the substance, in the corresponding place of the body there occurs a break, the "break-away": from the surface of the body there separates a plate of material and it is separated from the remaining body, departing from the surface with a defined speed. Thus, for instance, steel during pulse loads is destroyed by forces of order of 30,000 kg/cm^2.

§ 12. Experimental Methods of Detecting the Shock Adiabat of Solids

The laws of conservation of mass and momentum (11.31) and (11.32) connect between themselves the four parameters of the front of a shock wave: speed of propagation of a shock wave through an undisturbed substance D, jump of mass speed u, equal to the speed of a compressed substance with respect to an undisturbed one, pressure p, and specific volume V (or density $\rho = 1/V$). If we measure during the experiment the speeds D and u, by formulas (11.31) and (11.32) we can find pressure and volume, and then, using the equation of energy (11.34), we can calculate specific internal energy ε.

Thus, the problem of detecting all mechanical parameters of the front of a shock wave reduces to experimental determination of any two of them, in particular those most accessible for measurement of kinematic parameters: speeds D and u.

Speed of front D can be measured by experiment comparatively simply, recording the moments of passage of the front of the shock wave through known coordinate points, spaced from each other at an assigned distance. Measurement of the jump of mass speed u by such a direct form from the experimental point of view is much more difficult; therefore, for finding the second parameter we revert to various indirect methods, using for this purpose certain mechanical considerations.

The experimental methods described below on the investigation of compressibility of solids with the help of powerful shock waves and measurement of front parameters were proposed and developed by L. V. Al'tshuler, K. K. Krupnikov, B. N. Ledenev, and A. A. Bakanova [1-5], and also by the American authors Walsh and Christian et al. [22-26] (the latter did not include the method of "braking"; see below). However, Soviet scientists investigated a much wider range of pressures, to 4 million atmospheres.

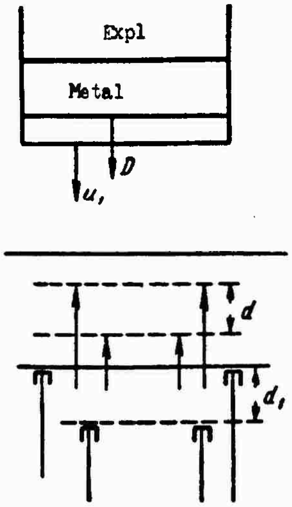

Fig. 11.18. Diagram of an experiment with the method of "break-away."

The concept of the use of the measurement of kinematic parameters for the purpose of studying shock adiabat, independent of previous researchers, was developed by F. A. Bauma, K. P. Stanyukovich, and B. I. Shekhter [21], who conducted measurements with comparatively weak shock waves.

In [1-3] there are described three methods of measurement of parameters of a shock wave, the essence of which we shall now expound.

1. Method of "break-away." It is based on the measurement of speed of the free surface of a body that is unloading after emergence at the surface of a shock wave, and on the application of the rule of doubling of speeds, according to which the mass speed u is approximately equal to half the speed of the free surface u_1. This method has a limited application, since at very large pressures there begin noticeable deviations from the rule of doubling, which leads to experimental errors in the determination of u. A fundamental diagram of the experiment consists in the following.

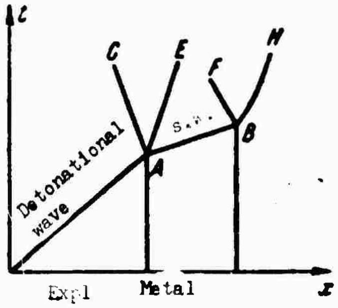

Fig. 11.19. x, t-diagram for "break-away" experiment.

The explosive charge touches the flat plate of investigated material, as shown in Fig. 11.18 (a corresponding diagram of motion on planes x and t is depicted in Fig. 11.19). When the detonational wave emerges from the VV on the boundary with the metal, there occurs disintegration of discontinuity; through the metal with speed D passes a shock wave (line AB), the speed of the contact boundary between VV and the metal (line AE) is equal to the mass speed of the metal u (through VV spreads reflected wave AC). After emergence of shock wave on free surface (point B) there again occurs disintegration of discontinuity, unloading wave BF runs back through the sample, and the boundary of the metal picks up doubled speed $u_1 \approx 2u$ (line BH). For measurement of speed of front D in [1-5] at defined distances inside a sample, as shown in Fig. 11.18, there were placed electromechanical transducers, which closed at moments of passage of the front of the wave and sent a pulse that was recorded with the help of a special electrical circuit and oscillograph.

Dividing distance d by time, it was possible to find the average speed of the front on the "base" of measurement of d (d bases were on the order of 5-8 mm, speed D ~ 5-10 km/sec, time ~10^6 sec. This demanded the development of special methods of registration of such short times). Likewise, with the help of electromechanical transducers there were also measured moments of passage through assigned coordinate points of the boundary of an unloaded substance* (see Fig. 11.18). The electrocontact

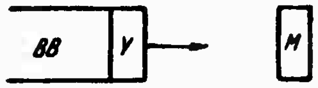

Fig. 11.20. Diagram of experiment with the method of braking.

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*For protection from closing of transducers by the air shock wave which "chases" the boundary of the metal, the transducers were equipped with protective caps.

method of measurement of speeds was proposed by V. A. Tsukerman and K. K. Krupnikov. Shock adiabat of iron was measured in this way to pressures of p ~ 1.5 • 10^6 atm (D ~ 7.5 km/sec, u ~ 2.4 km/sec).

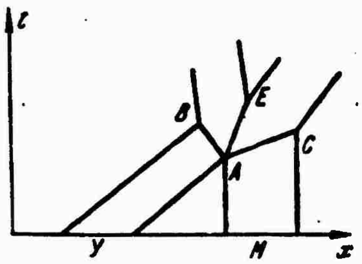

Fig. 11.21. x, t-diagram for the experiment with braking.

The method of "break-away" is not suitable for the investigation of porous materials, since in this case the additional speed u' during unloading is considerably less than speed u and the rule of doubling does not apply.

2. Method of "braking." For the study of more powerful shock waves, for which the rule of doubling of speeds introduces a noticeable error, the authors of [1] used another method which they called the method of "braking."

This method in principle is absolutely exact and useful for the study of any materials, including porous.

In this method with the help of a charge the VV accelerates to speed w of a plate made from the investigated material. The plate (striker) strikes another, stationary plate (target) made from the very same material. A diagram of the experiment is shown in Fig. 11.20, and diagram x, t in Fig. 11.21. At the moment of impact there appear two shock waves that spread through both bodies (AB and AC on diagram x, t). Pressures p and mass speeds u on both sides of the contact boundary between bodies are identical and are equal to the same magnitudes on the front of both shock waves as long as the latter do not reach the other boundaries of the samples.* The same

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*See § 24 in Chapter I.

speed u is also possessed by the contact boundary itself (line AE). Profiles of pressures and speeds after impact are depicted in Fig. 11.22.

By virtue of the identity of materials both shock waves are also identical, i.e., the jumps of mass speeds in both waves are equal. For the target, the speed jump also coincides with the speed of the compressed substance u, inasmuch as the target was initially at rest. Regarding the striker, however, in front of the shock wave the substance moves with the speed of flight of the striker w, and behind the wave, with speed u, so that the jump of speed in absolute value is equal to w - u. Consequently, w - u = u and u = w/2. Thus, the problem reduces to the measurement of front speed D in the target and the speed of flight of the striker w. This problem is experimentally solved the same as in the method of "break-away," with the help of a system of electromechanical transducers.

By the method of braking in [1] the shock adiabat of iron was taken up to pressures $p \sim 5 \cdot 10^6$ atm ($D \sim 12$ km/sec, $u \sim 5$ km/sec, $V_0/V \sim 1.75$). Also investigated was porous iron with a density 1.4 times less than normal.

The braking method can also be extended to the case when the investigated target and striker are made from different materials; however, the material of the striker in this instance must have a known shock adiabat. In a number of cases this turns out to be more expedient than to make the striker form the investigated material, since by means of corresponding selection of the striker material it is possible from the same VV charge to obtain a more powerful shock wave in the investigated substance.

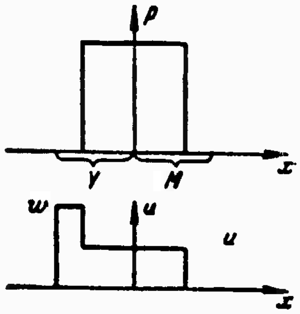

Fig. 11.22. Profiles of pressure and speed after impact in the method of braking.

If the materials of the striker and target are different, then in spite of the equality of pressures in both shock waves, the jumps of speeds are no longer identical, so that $w - u \neq u$.

However, if the shock adiabat of the striker is known, the dependence of pressure on jump of mass speed is known, i.e., function $p = f(w - u)$. On the other hand, pressure p is connected with jump of mass speed in the target, equal to the speed of contact boundary u, by formula (11.32): $p = Du/V_0$.

Measuring, as we did earlier, the speed of the shock wave in the target and the speed of the striker w, we can find speed u from the equation

$$f(w-u)=\frac{Du}{V_0}. \tag{11.45}$$

For this purpose it is very convenient to use the graphic method based on the utilization of the pressure — speed diagram (see § 24, Chapter I). These diagrams are widely applied in examining different processes with shock waves, in which there participate two contacting media, since on the contact boundary between media the pressures and speeds are identical.

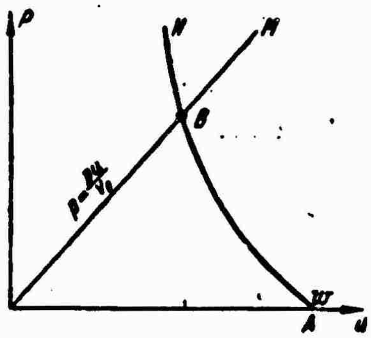

Fig. 11.23. p, u-diagram for the experiment with braking. HBA — shock adiabat of striker. OBM — locus of target states after impact.

We shall consider the collision of a striker and target with the help of diagram p, u, where u is the mass speed of the substance in the laboratory system of coordinates, in this case in the system in which the target is stationary in the beginning. In Fig. 11.23 the initial states of the target ($p = 0$, $u = 0$) and the flying striker $p = 0$, $u = w$ are depicted by points O and A. If the measured speed of the shock wave on the target is D, the locus of states of the target material in the shock wave is line $p = \frac{D}{V_0} u$ with known slope D/V_0. Let us depict the shock adiabat of the

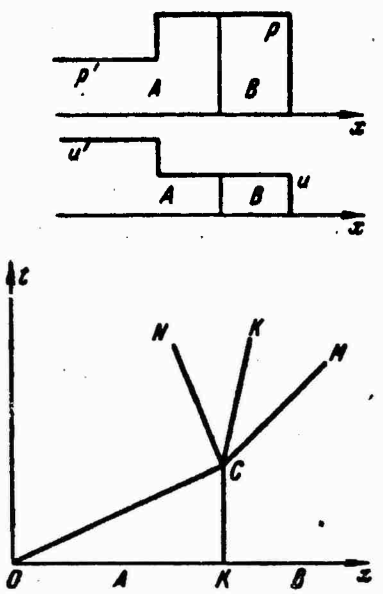

Fig. 11.24a. Profiles of pressure and speed and x, t-diagram for the experiment with reflection. The case when the reflected wave is a shock wave. OC — shock wave in A, CM — shock wave in B, CN — reflected shock wave in A, KCK — line of contact A and B.

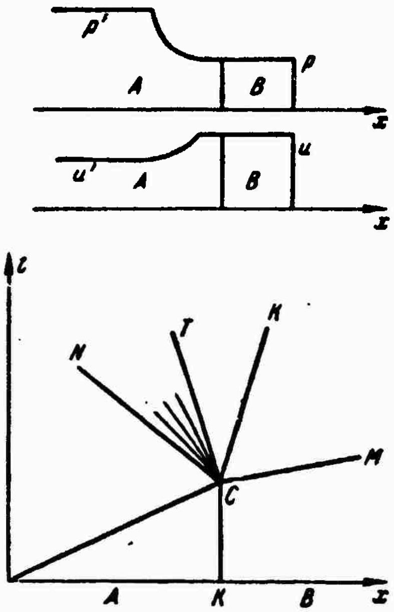

Fig. 11.24.b. Profiles of pressure and speed and x, t-diagram for the experiment with reflection. The case when the reflected wave is a wave of rarefaction. OC — shock wave in A, CM — shock wave in B, CN — head of rarefaction wave, CT — tail of rarefaction wave, KCK — line of contact A and B.

substance of the striker, considering the dependence of pressure not on volume, but on the jump of speed, equal in this case to w - u: $p = f(w - u)$. The point of intersection B of both lines, according to equation (11.45) also determines the state (pressure and mass speed) in both shock waves. If the striker and target are made from one material, then as we already know, the point of intersection lies exactly in the middle between the abscissas of points O and A $(u = w/2)$.

3. Method of "reflection." This method uses the regularities followed by the process of disintegration of an arbitrary discontinuity appearing during the reflection of a shock wave from the boundary of two media (see § 24 in Chapter I). It possesses the advantage, as compared to the preceding method, that it does not require the measurement of mass speeds, which in the experimental aspect is much more complicated than the measurement of speed of the front of a shock wave. However, for this method it is necessary to have a standard substance with a known equation of state. The method was developed by the authors of [2] jointly with G. M. Gandel'man.

Let us consider the transition of a strong shock wave from medium A to medium B. Through substance B there always passes shock wave and the reflected wave in A can be either a shock wave, if substance B is "harder" than A, or a wave of rarefaction, if B is "softer" than A (this is the simplest of all to represent, if we consider these limiting cases: A — gas, B — solid, and A — solid, B — gas).

Profiles of speeds and pressures in both cases are depicted in Fig. 11.24a and b. In the same place there are given corresponding diagrams x, t. The notations made in Fig. 11.24 need no explanation.

Let us consider this process with the help of the diagram pressure — speed (in the initial state both substances, A and B, are stationary in the laboratory system of coordinates).

Let us assume that the equation of state of substance A is known. Let us depict on the p, u-diagram (Fig. 11.25) the shock adiabat of substance A, $p_A(u)$, for the first shock wave spreading through the undisturbed material. If we measure in the experiment the speed of the front of the initial shock wave D_1, the state in it will be depicted by the intersecting point of line $p = D_1u/V_{0A}$ with shock adiabat $p_A(u)$ (point a $(p_a u_a)$).

After the reflection of this shock wave from the boundary between media A and B in substance A there appears a new state. If the reflected wave is a shock wave, the state lies on the shock adiabat of secondary compression, for which state $a(p_a, V_a, u_a)$ is initial; this shock adiabat is depicted by curve p_H which passes upwards from point a.

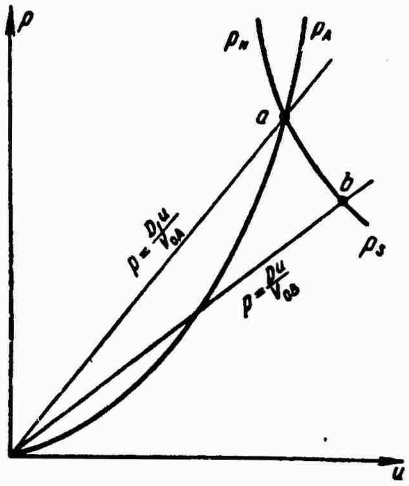

Fig. 11.25. p, u-diagram for the experiment with reflection.

If, however, the reflected wave is an adiabatic wave of rarefaction, the new state lies on the isentrope of rarefaction, proceeding downwards from point a (curve p_s). Inasmuch as the equation of state of substance A is assumed to be known, both the shock adiabat of secondary compression $p_H(V, V_a, p_a)$, and also the isentrope of rarefaction with entropy equal to $S_a = S(p_a, V_a)$, can be converted in such a manner so that instead of the volume, speed enters as the argument. In the first case this is done by means of the use of the relationships on the front of the shock wave, and in the second with the help of the relationships that are valid for the rarefaction wave (see § 10 in Chapter I).

If we also measure in the experiment the speed of the shock wave in medium B - D, the locus of states in this wave is line $p = Du/V_{0B}$. Point of intersection b of this line with curve $p_H a p_s$ is the locus of possible states in substance A after reflection of the shock wave, and it determines the pressure and speed in the shock wave at B, equal to the pressure and speed of the contact boundary of A and B (see Fig. 11.24).

Diagram p, u in Fig. 11.25 depicts a second case when during reflection there appears a wave of rarefaction. In the first case the line $p = Du/V_{0B}$ passes higher than line $p = D_1u/V_{0A}$ and the point of intersection b lies higher than point a on the shock adiabat of secondary compression of substance A, which is described by the curve ap_H.*

Thus, the method of "reflection" consists of the following. In the plate from material A with a known equation of state there is created a shock wave either directly from the VV charge, or by means of impact of the other plate, preliminarily accelerated by the VV to a high speed. This wave emerges in samples of investigated materials B, which also includes the sample from material A (diagram of the experiment is shown in Fig. 11.26). By recording the moments of closing of the electromechanical transducers located in the places shown in Fig. 11.26 by the arrows, we determine the speeds of the front D_1 and D. Constructing the shock adiabat $p_A(u)$ on the p, u-diagram and drawing line $p = D_1u/V_{0A}$, we find point a, i.e., the state in the shock wave in A. We then draw the shock adiabat of secondary compression through point a upwards, and downwards we draw the usual adiabat and plot line $p = Du/V_{0B}$, thereby determining the unknown state b(p, u) in the shock wave in the investigated sample.

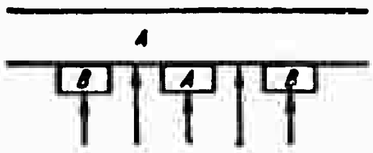

Fig. 11.26. Diagram of the experiment with reflection.

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*Hence, incidentally, one may see what magnitude is characterized by the "hardness" of the substance. Let us assume that the shock waves are not very strong and their speeds are close to speeds of sound: $D \approx c_B, D_1 \approx c_A$. Substance B is harder than A, and the reflected wave is a shock wave if $c_B/V_B > c_A/V_A$ or $\rho_B c_B > \rho_A c_A$.

Magnitude ρ_c is sometimes called acoustic impedance. It determines the connection of pressure and speed in an acoustic or weak shock wave: $p = \rho cu$.

Actually (in the experiment) the changes of pressure between states a and b always were small. In these conditions, as shown by calculations curve $p_H a p_S$ with great accuracy can be represented as a mirror transformation of shock adiabat of primary compression at point a. Let us note that the slope of curve $p_H a p_S$ at point a is determined by the speed of sound behind the front of the primary shock wave in A. Actually, in a wave of rarefaction, just as in a weak compressional wave, $dp = \pm \rho c\, du$ (see formula (1.59)), i.e., the slope of curve $p_H a p_S$ at point a is $\left|\frac{dp}{du}\right| = \rho c = \frac{c}{V}$, where c and V is the speed of sound and volume in substance A, compressed by the first shock wave. Methods of experimental determination of the speed of sound behind the front of a shock wave will be considered below.

By the method of reflection in the work of L. V. Al'tshuler, K. K. Krupnikov, and M. I. Brazhnik [2] shock adiabats of a large number of metals (Cu, Zn, Pb, and others) were taken. The method was used for the study of compressibility of sodium chloride in [5], and also was applied in many works of foreign scientists. Most frequently the materials of shield A were iron, aluminum, or brass.

§ 13. Extraction of a Curve of Cold Compression from the Results of Experiments on Shock Compression

One of the most valuable results of experiments on shock compression of solids is the determination of curves of cold compression of the substance $p_x(V)$, which characterize the repulsive forces between atoms of the body. Functions $p_x(V)$ and $\varepsilon_x(V)$ are found by means of theoretical treatment of experimental data on the shock adiabat of the substance. For finding the curve of cold compression in a wide range of compressions and pressures in [3] there were used trinomial presentations of thermodynamic functions p(V, T) and ε(V, T) (11.30). Electron member p_e and ε_e were notated on the basis of purely theoretical considerations (see §§ 5 and 6), where for the coefficients of electron heat capacity β_0 known experimental values were taken.

Taking experimental dependences p(V) and ε(V) along the shock adiabat, relationship (11.30) may be considered as two equations with respect to three unknown functions p_x(V), G(V), and T(V), where T(V) is the dependence of temperature on volume along the shock adiabat.

As the third, missing equation it is possible to use the connection between the Grueneisen coefficient G(V) and the curve of cold compressibility p_x(V), which is given by the Slatter-Landau formula (11.18).* The numerical solution of this system of equations gives the curve of cold compression p_x(V), function G(V), and temperature in the shock wave T. The data in Table 11.2 and on the graphs in Fig. 11.8 (§ 7) were also obtained in this way.

Specific results for other metals under investigation can be found in the tables of [3].

If we know from experiment the shock adiabats for porous and solid substances, it is possible to do without the use of the connection between functions G(V) and p_x(V). Namely, considering not too high temperatures and disregarding electron members p_e and ε_e,

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*In a number of cases a somewhat different connection was used between functions G(V) and p_x(V), which is given by the Dugdale-McDonald formula [27].

it is possible to write:

$$\frac{1}{\Gamma}=\frac{\Delta\varepsilon_T}{V\Delta p_T}=\frac{1}{V}\,\frac{\varepsilon_{\text{порист}}(V)-\varepsilon_{\text{сплош}}(V)}{p_{\text{порист}}(V)-p_{\text{сплош}}(V)},$$

where the magnitudes in the right part are the experimental values on shock adiabats of a solid and porous substance during their compression to the same volume. The elastic components of pressure and energy in both cases are identical, so that the differences of ε and p are equal to the excesses of purely thermal energy and pressure in the compressed porous substance as compared to the compressed solid substance.

In this way in [1] there was obtained the curve of cold compressibility of iron (it is depicted in Fig. 11.2 in § 2).

In [5] there was found the curve of cold compression of sodium chloride. Comparison with expressions for repulsive forces in ionic crystals permitted the determination of the parameters entering these formulas, characterizing the force of interaction.

The method of calculation of temperature of shock adiabat in waves of comparatively low amplitude, when thermal members are small as compared to elastic, and shock adiabat closely coincides with the curve of cold compression, is described in [22] (electron members naturally are not considered here).

For an analytic description of shock adiabat and curve of cold compression of a suvstance $p_x(V)$ they frequently use interpolation formulas of a different type. For this, functions of a defined form are given, containing several parameters, which are determined with the help of some experimental data. An example could be the widely used formula $p_x = A[(V_0/V)^n - 1]$, containing two parameters, A and n. In [5] during the investigation of sodium chloride, curve $p_x(V)$

was obtained in analytic form by means of the use of a power or exponential presentation for repulsive forces in ionic crystals. The constants entering the expression were determined by means of comparison with data on dynamic compressibility.

S. V. Kormer and V. D. Urlin [14] constructed an interpolation formula for the curve of cold compression in the form

$$p_x = \sum_{n=1}^{6} a_n \left(\frac{V_{0x}}{V}\right)^{\frac{n}{3}+1}.$$

Coefficients a_n were determined without the use of experimental data on shock compression only from the conditions of the connection of the coefficients with known parameters of normal state (compressibility, Grueneisen coefficient, and others) and the condition that at large pressures the curve is closed with the dependence following from the model of Thomas, Fermi, and Dirac. A good coincidence was obtained with curves $p_x(V)$, extracted from the experiment.*

3. Acoustic Waves and Splitting of Waves

§ 14. Static Deformation of a Solid

Above, during the study of shock compression of solids, it always was assumed that pressure in a compressed substance is isotropic, and has a hydrostatic character, as in a liquid or gas. Increase of density was considered as the result of manifold compression of the substance. Correspondingly, the elastic properties of the substance

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*In the future S. B. Kormer, V. D. Urlin, and L. T. Popov [15] improved this method, adding to the series one more member with the use of one experimental point on shock adiabat. Very good coincidence with experimental curves was obtained.

were characterized only one magnitude, compressibility $\varkappa = -\frac{1}{V} \left(\frac{\partial V}{\partial p}\right)_s$, which determined the speed of "sound":

$$c_0 = \sqrt{-V^2\left(\frac{\partial p}{\partial V}\right)_S} = \sqrt{\frac{V}{\varkappa}}.$$

Thus it is possible to proceed only when pressures are sufficiently great, and the effects, connected with the strength of solids and the existence of shear strains and stresses, do not play a part. If loads are small, it is necessary to take into account the elasticity properties of the solid, distingusihing it from a liquid. This essentially affects the character of dynamic processes and in particular the propagation of elastic compressional and rarefaction waves. Thus, it turns out that in a solid, acoustic waves can spread with different speeds, depending upon the specific conditions. Before we consider these dynamic phenomena, let us see how a solid behaves during static loads. Let us consider that deformations and loads are small, so that the linear theory of elasticity is valid.

The state of the deformed body is described by two tensors: tensor of deformations and tensor of stresses. Subsequently we shall mention only a few simple cases of uniform deformations (when each element of the body is deformed in an identical manner), which are characterized by simple and graphic magnitudes. Therefore we shall not introduce the tensor of deformation in the common form.*

The component of the tensor of stresses σ_{ik}, where indices i and k designate coordinate directions x, y, z, constitutes a projection on the i-th axis of the force which acts on a single spot in the body with the direction of the normal along axis k. Components σ_{xx}, σ_{yy}, σ_{zz} constitute normal stresses, and σ_{xy}, σ_{xz}, σ_{yz} are tangential or shear

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*See, for example, the book by L. D. Landau and Ye. M. Lifshits [28].

(Fig. 11.27). Tensor σ_{ik} is symmetric, i.e., $\sigma_{xz} = \sigma_{zx}$, $\sigma_{yz} = \sigma_{zy}$, $\sigma_{xy} = \sigma_{yx}$.

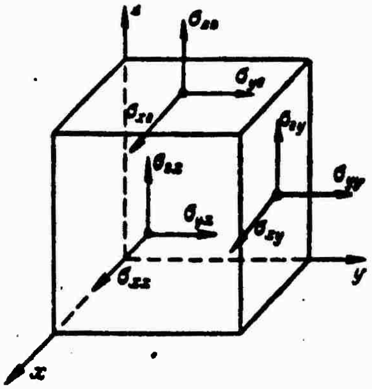

Fig. 11.27. Diagram illustrating the meaning of components of tensor of stresses.

Let us consider several examples of deformations.

1. Let us imagine a cylindrical rod of length L and diameter d, to the ends of which there is applied a compressing force, i.e., pressure p. Axis z will be directed along the axis of the rod, as shown in Fig. 11.28. Lateral surface of rod is assumed to be free. Under the action of a load the rod is shortened to length ΔL and is thickened (diameter is increased to Δd).

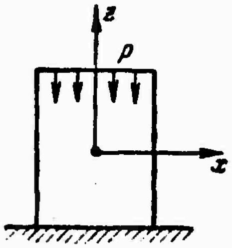

Fig. 11.28. Diagram of compression of a rod.

In this case only the normal stress in axial direction σ_{zz} is different than zero; it is equal to external pressure $\sigma_{zz} = p$. Normal stresses in transverse directions σ_{xx}, σ_{yy} are absent, since the lateral surface of the rod is free and nothing prevents the rod from expanding in this direction. Tangents or shear stresses σ_{xy}, σ_{xz}, σ_{yz} in the selected system of coordinates also are equal to zero, which is obvious.

According to Hooke's law during small deformations, relative shortening of a rod is proportional to the applied force:

$$\frac{\Delta L}{L} = \frac{p}{E} = \frac{\sigma_{zz}}{E}, \qquad (11.46)$$

where E is Young's modulus (this is the definition of Young's modulus).

Relative thickening of the rod is proportional to relative shortening:

$$\frac{\Delta d}{d} = -\sigma \frac{\Delta L}{L}, \qquad (11.47)$$

where σ is Poisson's ratio.

Poisson's ratio is always positive and less than 1/2. This follows from the fact that during compression of the rod the latter becomes thicker, where by its volume can then only be reduced, but not increased (at constant volume d^2L = const, $\Delta d/d = -1/2\ \Delta L/L$, $\sigma = 1/2$).

2. Let us assume that the lateral surface of a rod is pressed in such a manner that during axial compression the rod cannot be deformed in transverse direction (rod is placed in a case with hard walls). There then appear normal stresses in transverse direction $\sigma_{xx} = \sigma_{yy}$, which exactly balance the external lateral force on the walls of the case.

Normal axial stress σ_{zz}, as before, is equal to external compressing pressure p. The theory of elasticity proves that relative shortening of a rod, during axial deformation from all sides, is connected with external pressure by a relationship analogous to (1.46):

$$\frac{\Delta L}{L} = \frac{p}{E'} = \frac{\sigma_{zz}}{E'}, \tag{11.48}$$

where

$$E' = \frac{E(1-\sigma)}{(1+\sigma)(1-2\sigma)}. \tag{11.49}$$

Magnitude E' is always greater than Young's modulus E: in order to shorten a rod, pressed on the side just as a free one, it is necessary to apply to it a large compressing force. Normal stresses in transverse directions are equal to

$$\sigma_{xx} = \sigma_{yy} = \frac{\sigma}{1-\sigma}\sigma_{zz} = \frac{\sigma}{1-\sigma}p. \tag{11.50}$$

Tangential stresses in the selected system of coordinates are absent. All relationships in the two considered examples are also valid in case of extension of the rod.

3. During manifold compression (and expansion) the body changes volume, preserving its form, i.e., remains similar to itself. In order to carry out manifold compression, to the surface of the body it is necessary to apply constant pressure. The stress tensor during manifold compression is diagonal ($\sigma_{xy} = \sigma_{xz} = \sigma_{yz} = 0$); all three normal components are identical and are equal to pressure. This takes place with any selection of the system of coordinates. "Pressure" in the body in this case is "isotropic" and has a hydrostatic character, as in a liquid.

During small deformations the relative change of volume* is proportionate to pressure:

$$\frac{\Delta V}{V} = -\varkappa p = -\frac{p}{K}, \tag{11.51}$$

where $\varkappa$ is compressibility, and the reciprocal $K = 1/\varkappa$ is the modulus of manifold compression.

4. Let us further consider the deformation of pure non-dilatational strain in one direction, as shown in Fig. 11.29. During pure non-dilatational strain the body only changes its form, but does not change volume. In the example shown in Fig. 11.29, only one tangential stress σ_{xz} is different than zero. All remaining components of the tensor of stresses are equal to zero. According to Hooke's law the angle of strain is proportional to shearing force τ (per

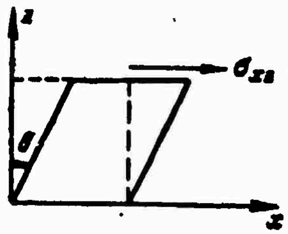

Fig. 11.29. Deformation of pure non-dilatational strain in one direction.

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*The sum of diagonal components of a strain tensor is equal to $u_{xx} + u_{yy} + {}_{zz} = \Delta V/V$. With multilateral compression $u_{xy} = u_{yz} = u_{xz} = 0$.

unit of area), which is equal to stress σ_{xz}:

$$\theta \approx \operatorname{tg}\theta = \frac{\tau}{G} = \frac{\sigma_{xz}}{G}, \qquad (11.52)$$

where G is the shear modulus.

As we know (see [28]), arbitrary strain can be presented in the form of the sum of shearing strains and multilateral compression (expansion). Owing to such an internal bond of strains of unilateral compression of the rod and elementary strains of multilateral compression and shear, the four characteristics of the material E, σ, K, G, are not independent, and are connected together by two relationships.

It is possible to show (see for example [28]) that

$$E = \frac{9KG}{3K+G}, \quad \sigma = \frac{1}{2}\,\frac{3K-2G}{3K+G}, \qquad (11.53)$$

and conversely,

$$G = \frac{E}{2(1+\sigma)}, \quad K = \frac{E}{3(1-2\sigma)}.^{*} \qquad (11.54)$$

Thus, Hooke's law for unilateral strain of a rod pressed from the sides (11.48) can be written thrugh moduli K and G in the form

$$\frac{|\Delta L|}{L} = \frac{p}{E'}, \quad E' = K + \frac{4}{3}G. \qquad (11.55)$$

For orientation in the numerical values of the parameters of the material we shall indicate that for iron (treated with 1% carbon)

$$E \approx 2{,}1\cdot 10^{6}\ \text{kg/cm}^2, \quad G \approx 0{,}82\cdot 10^{6}\ \text{kg/cm}^2,$$
$$K \approx 1{,}61\cdot 10^{6}\ \text{kg/cm}^2, \quad \sigma \approx 0{,}28.$$

During multilateral compression or extension of a body in any coordinate system the stress tensor is diagonal and all three of its components are identical. During other strains the stress tensor is

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*From the formula it is clear that $\sigma \leq 1/2$, since $K > 0$.

diagonal and tangential stresses are absent only in certain specially selected coordinate systems. An example of this is the above-considered compressive strain of a rod: free and pressed on the side. Inequality of diagonal elements of the stress tensor is connected with the fact that in reality the strain is not multilateral compression (extension) and contains a shear element. This appears in evident form, if we change to another system of coordinates or, the same, consider the forces acting on an area slanted to the axis of the rod. It immediately becomes clear that slanted areas experience tangential stresses, which testifies to the existence of shearing strains.

We shall calculate tangential stress acting on an area that is inclined towards the direction of action of external pressure at an angle of 45° (Fig. 11.30). For simplicity we shall consider not a cylindrical rod, but a flat layer, infinite in direction y and pressed on the side so that in direction x there are no displacements. In the system of coordinates x, y, z there are tensions σ_{zz} and $\sigma_{xx} = \sigma_{yy}$. In order to find the tangential stress acting on plane AB we shall introduce a new system of coordinates x' y' z', inclined with respect to the old system along axis y (axis y and y' coincide). By the rule of conversion of tensors or turn of system of coordinates we find

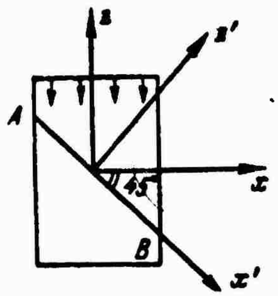

Fig. 11.30. Concerning the question of nondiagonality of a stress tensor.

$$\sigma_{x'z'} = \sigma_{zz}\cos^2 45^\circ - \sigma_{xx}\cos^2 45^\circ = \frac{1}{2}(\sigma_{zz} - \sigma_{xx}).$$

This is the tangential stress in the direction of axis x' on area AB, the normal to which is directed along axis z'.

§ 15. Transition of a Solid to a Fluid State

One of the characteristic properites of a solid, distinguishing it from a fluid, is the form stability of the solid and shear resistance. A fluid has no shear resistance and takes on any form with ease as long as its volume (density) is not changed. Tangential shearing stresses in a fluid are absent in static state.*

A fluid is characterized by zero shear modulus $G = 0$. Formally, when $G = 0$ Poisson's ratio, according to formula (11.53), is equal to $\sigma = 1/2$. The stress tensor in any system of coordinates is diagonal where all three of its normal components are identical and are equal to "hydrostatic" pressure, which is "isotropic." Elastic properties of a fluid are characterized only by its compressibility or modulus of multilateral compression.

It is known that during sufficiently large loads, not leading to multilateral compression, a solid changes its elastic properties and becomes plastic, fluid, and in a certain respect similar to a fluid.

Fluid state of a solid is characterized not by the complete absence of tangential stresses, as in a fluid, but by the absence of growth of tangential stresses with the growth of shearing strains. Starting from certain critical shear strains and tensions, a solid ceases to resist further increase of shear.

Above, the shear modulus G was defined as a proportionality factor between tangential stress during pure strain and shearing strain (see formula (11.52)). By virtue of the linearity of the dependence of tension and strain the increases of strain and tension simultaneously are also proportional:

$$\sigma_{xz} = G\theta, \; d\sigma_{xz} = G\,d\theta$$

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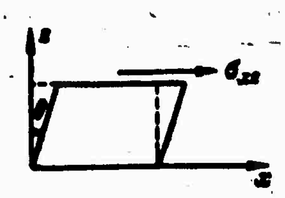
*They appear only at the time of change of form and depend not on the strains themselves, but on the speed of their change.



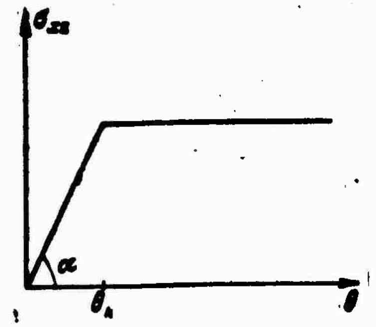


Fig. 11.31. Tangential stress-shear angle diagram.

(during pure strain at angle θ, as shown in Fig. 11.29).

In the fluid state of a solid, after strain θ and tension σ_{xz} becomes greater than critical θ_{crit}, σ_{crit}, further growth of tension with increase of strain is ceased (or is sharply retarded). This is illustrated by the diagram of $\sigma_{xz}(\theta)$ in Fig. 11.31. If we formally define shear modulus in this state as the proportionality factor between increases of $d\sigma_{xz}$ and $d\theta$, but not between the magnitudes σ_{xz} and θ themselves, it should be put equal to zero.

Let us consider unilateral compression of a non-fluid and fluid body. Let us assume that a body of cylindrical form is placed in a cylindrical vessel with rigid walls and is compressed by a piston along its axis (Fig. 11.32). Let us depict schematically how the atomic arrangement of the body changes (Fig. 11.33). We shall consider the lattice for simplicity to be cubic. If the body is non-fluid, the interatomic distances in direction of the axis are reduced, and in transverse directions they remain constant; the atoms then remain at "their places." This is shown in Fig. 11.33b.

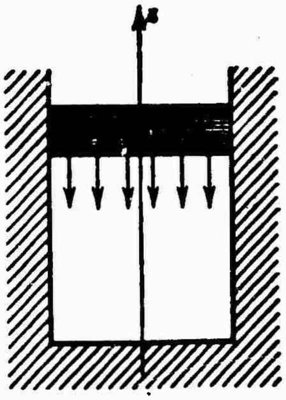


Fig. 11.32. Diagram of unilateral compression of a rod.

If, however, the body is fluid, all interatomic distances are reduced, there occurs reconstruction of the lattice, and such redistribution of atoms that the lattice even in a compressed state remains cubic (Fig. 11.33c). For clarity, the "atoms" in Fig. 11.33 are renumbered.*

The first case (Fig. 11.33b) contains the strain element. Actually, in an unstrained state (Fig. 11.33a) the projection of atom 2 on slanted plane AB, passing through atoms 1-6 of two adjacent horizontal rows, descends to point C, located in the middle of segment AB. During strain of a non-fluid body (Fig. 11.33b) point C shifts nearer to point B. Slanted rows of atoms shift with respect to one another: upper row 2-7-12 shifts with respect to lower row 1-6-11 to the right and downwards.

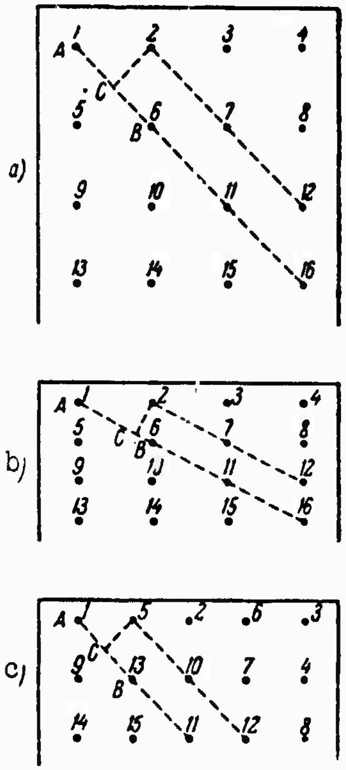


Fig. 11.33. Diagram illustrating the strain of a non-fluid (b) and fluid (c) body; a-unstrained state.

During strain of a fluid body the lattice is cubic as before, and the projection of atom 5 on slanted plane AB passes through atoms 1-13; point C, as also in the unstrained state, lies in the middle of segment AB. Slanted rows of atoms 5-10 and 1-13 do not shift with respect to one another, as also in the unstrained state.

During strain the body obtains elastic energy due to the work of the external forces producing the strain. If the body is non-fluid this energy is connected both with change of volume and also with shear. At a given volume the elastic energy is minimum, is compression is multilateral and there are no shearing strains. Therefore, during

---

*It does not follow, of course, to think that shift of the defined atoms occurs precisely as shown in Fig. 11.33.

unilateral compression of a non-fluid body to a give volume the body is in a nonequilibrium state. Equilibrium state at given volume would correspond to multilateral compression, i.e., a reconstructed crystal lattice.

For lattice reconstruction there is needed an "activation energy" and the atoms must surmount the potential barriers.* During small loads reconstruction does not occur and the solid behaves, with respect to strain, as a non-fluid body.

However, during sufficiently large loads a hard body loses its "hardness" and fluidity, and assimilates to a fluid, i.e., it acquires the ability to be reconstructed in such a way that its energy at a given volume is minimum.

In particular, during unilateral compression of a body, this happens when the tangential stress in a plane, inclined at an angle of 45° to the direction of the compressing force $\sigma_{x',z'}$ (see end of preceding paragraph), exceeds the limit, i.e., critical shear strain σ_{crit}.

Noting that

$$\sigma_{x'z'} = \frac{1}{2}(\sigma_{zz} - \sigma_{xx}) = \frac{1}{2}\,\frac{1-2\sigma}{1-\sigma}\,\sigma_{zz} = \frac{1}{2}\,\frac{1-2\sigma}{1-\sigma}\,p,$$

we find the critical compressing load p_{crit}, above which there occurs transition of the body into fluid state:

$$p_{cr} = \frac{1-\sigma}{1-2\sigma}\,2\sigma_{cr}. \qquad (11.56)$$

In distinction from the thermodynamic constants of the substance (Young's modulus or compressibility), critical shear strain, as a magnitude characterizing strength, strongly depends on the treatment of the metal, impurities, etc. For iron approximately $\sigma_{crit} = 600$ kg/cm^2, $p_{crit} = 1900$ kg/cm^2.

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*Possibly, reconstruction is connected with macroscopic breaking of particles of the body.

Let us consider unilateral compression of a body in direction z under the action of compressing force p. In transverse directions x, y there are no strains (rod is pressed from the side). We shall formally write out the transition from non-fluid to fluid state, considering, in the law of proportionality between increases of tension and strain, the shear modulus to be equal to zero during loads exceeding critical. By formulas (11.48) and (11.55) when $p = \sigma_{zz} < p_{crit}$

$$\sigma_{zz} = \left(K + \frac{4}{3}G\right)\frac{\Delta L}{L}, \quad \frac{d\sigma_{zz}}{d(\Delta L/L)} = K + \frac{4}{3}G.$$

By formulas (11.50) and (11.53)

$$\sigma_{xx} = \sigma_{yy} = \left(K - \frac{2}{3}G\right)\frac{\Delta L}{L}, \quad \frac{d\sigma_{xx}}{d(\Delta L/L)} = K - \frac{2}{3}G;$$

$$\sigma_{x'z'} = \frac{1}{2}(\sigma_{zz} - \sigma_{xx}) = G\frac{\Delta L}{L}, \quad \frac{d\sigma_{x'z'}}{d(\Delta L/L)} = G.$$

After the load attains its critical magnitude, we put $G = 0$ in the formulas for the derivatives from stresses (but not in formulas for the stresses themselves). When $p > p_{crit}$, we obtain:

$$\frac{d\sigma_{zz}}{d(\Delta L/L)} = \frac{d\sigma_{xx}}{d(\Delta L/L)} = K, \quad \frac{d\sigma_{x'z'}}{d(\Delta L/L)} = 0. \qquad (11.57)$$

Normal stresses σ_{zz}, σ_{xx}, σ_{yy} now grow equally in accordance with the modulus of multilateral compression (during unilateral compression $\Delta L/L = \Delta V/V$). Tangential stress in the slanted plane remains constant and equal to $\sigma_{x'z'} = \sigma_{crit}$ (critical strain is equal to $\left(\frac{\Delta L}{L}\right)_{crit} = \frac{\sigma_{crit}}{G}$). A stress-strain diagram is depicted in Fig. 11.34.

During loads less than critical and on the order of critical $\sigma_{zz} \neq \sigma_{xx}$ "pressure" has an essentially nonhydrostatic character. In the limit when loads are sufficiently great, $p \gg p_{crit}$, the relative

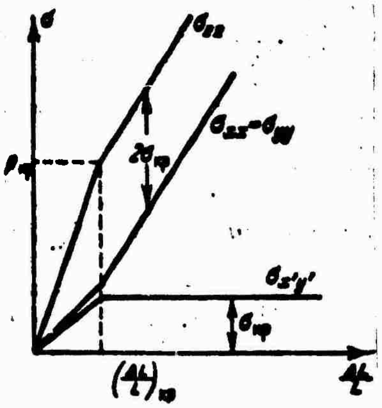

Fig. 11.34. Stress-strain diagram for unilateral compression of a body.

difference $(\sigma_{zz} - \sigma_{xx})/\sigma_{zz} = 2\sigma_{crit}/\sigma_{zz} \to 0$, i.e., all three normal stresses become almost identical. Tangential stress $\sigma_{x'z'} = \sigma_{crit}$ becomes small as compared to normal. It remains constant or slowly increases, much slower than before.

§ 16. Speed of Propagation of Acoustic Waves

We shall transfer the results of the preceding paragraphs to the case of dynamic loads and shall find the speed of propagation of acoustic waves of volume compression (and rarefaction) in different conditions.

Let us assume that to the end of a thin rod with a free lateral surface at the initial moment there is applied a constant compressing force, i.e., pressure p.*

Through the body there will run a compressional wave. We shall designate the speed of its propagation as c_1. The substance between the front of wave and the end is strained, as in example 1 of § 14, and obtains constant speed u in the direction of action of the force along the axis. As can be seen from Fig. 11.35, unit shortening of the rod in the compressed region is equal to $[c_1t-(c_1-u)t]/c_1t = u/c_1$.

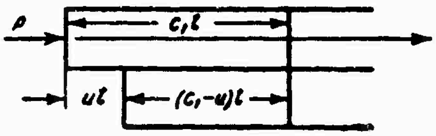

Fig. 11.35. Diagram illustrating the propagation of an acoustic compressional wave.

If we consider small loads and strains, according to Hooke's law

(11.46)

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*Such formulation of the problem is analogous to the problem concerning a piston, considered in gas dynamics (see Chapter I).

$$\frac{u}{c_1}=\frac{p}{E}\,{}^{*}). \qquad (11.58)$$

During the time t the mass of the substance, enveloped by the wave $\rho c_1 t$ (per unit of cross section of the rod), obtains momentum $\rho c_1 t u$, which according to Newton's law is equal to pt, so that

$$p=\rho u c_1 \qquad (11.59)$$

This formula is fully analogous to a corresponding formula in gas dynamics. From relationships (11.58) and (11.59) follows the expression for speed of propagation of compressional waves through a rod (speed of "sound"):

$$c_1=\sqrt{\frac{E}{\rho}}. \qquad (11.60)$$

With the same speed a wave of extension or wave of unloading is also propagated, if the compressing load is removed from the compressed rod.

Let us now imagine that the rod is pressed from its lateral face, as in example 2 of § 14, i.e., in the compressional wave the substance is not strained in the plane perpendicular to the direction of propagation of the wave.**

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*In a dynamic process, which is adiabatic, Young's modulus differs somewhat from the one used in statics and corresponding to isothermal conditions. This distinction is usually insignificantly small (see [28]). The same also pertains to Poisson's ratio and the modulus of multilateral compression. Adiabatic and isothermal shear moduli do not differ from each other, since shear is not accompanied by change of volume of the body.

**The rod may be considered free, but the time is considered in which the compressional wave passes a distance considerably less than the diameter. The wave of unloading from the lateral surface spreads to the axis with terminal velocity, so that to the considered time it embraces only the peripheral layer. In the central regions, close to the axis, there will still be no transverse displacements, and the strain of these layers will be unilateral.

case from normal stress with respect to volume. In the fluid state this derivative is proportional to the modulus of multilateral compression as if the shear modulus was equal to zero. Therefore, the speed of propagation of sufficiently strong acoustic compressional waves and rarefaction was is determined only by the compressibility of the material:

$$c_0=\sqrt{\frac{K}{\varrho}}=\sqrt{\frac{V}{\varkappa}}. \tag{11.62}$$

Speed c_l is sometimes called the speed of elastic waves, and speed c_0, the speed of plastic waves; c_0 is always less than c_l; for instance, in iron $c_l = 6.8$ km/sec and $c_0 = 5.7$ km/sec. The speed of propagation of strong compressional waves (shock waves) depends on the amplitude of the wave. It is always greater than c_0 or close to this magnitude. The speed of propagation of weak perturbations is always equal to c_l, independent of amplitude, inasmuch as perturbations spread with this speed only when they are small.

Questions of propagation of waves of rarefaction and compression in an elasto-plastic medium with a nonlinear dependence between stress and strain, similar to the dependence $\sigma_{zz}(\Delta L/L)$, which is shown in Fig. 11.34, was investigated in detail by Kh. A. Rakhmatullin. References to original works in this area may be found in the survey by Kh. A. Rakhmatullin and G. S. Shapiro [29].

In following paragraph we shall consider a simple case of propagation of waves with the shown properties of substance.

§ 17. Splitting of Compressional and Unloading Waves

Let us see what partically occurs, if to the surface of a flat body at the initial moment we apply constant pressure p. Let us consider pressure to be sufficiently small so that strain linearly

Repeating the preceding reasonings and using formula (11.55), we shall find the speed of "sound" for this case:

$$c_l = \sqrt{\frac{E'}{\rho}} = \sqrt{\frac{K + \frac{4}{3}G}{\rho}}. \qquad (11.61)$$

Speed c_l is nothing but the "longitudinal" speed of sound, i.e., the speed of propagation of longitudinal waves in an unlimited elastic medium.*

Actually, when a compressional wave is propagated through an unbounded medium, there are no displacements in the plane perpendicular to the direction of propagation, and the phenomenon occurs just as in the case of a rod pressed from the side.

Speed c_l is always greater than the speed of the wave in a free rod, since $E' > E$ (see § 14).

With speed c_l there spread only rather weak compressional waves (and rarefaction waves), in which "pressure," or more exact, normal stress, acting on the plane perpendicular to the direction of propagation, is quite small, less than critical, and determined by formula (11.56). If the wave spreads through an already stressed substance let us say, a wave of unloading), the absolute value of the stress drop should be less than critical (see in greater detail in § 17). If, however, the dynamic load is great and larger than critical, the compressed solid matter, as shown in the preceding paragraph, passes into a fluid state, similar to a liquid.

The speed of propagation of waves, as we know, is determined by the derivative of "pressure" with respect to volume, and in this

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*Speed of propagation of transverse waves, in which the displacements of particles are perpendicular to the direction of propagation of the wave and in which there occurs only shear strain, without compression and rarefaction, is equal to: $c_t = \sqrt{G/\rho}$; $c_t < c_l$.

case from normal stress with respect to volume. In the fluid state this derivative is proportional to the modulus of multilateral compression as if the shear modulus was equal to zero. Therefore, the speed of propagation of sufficiently strong acoustic compressional waves and rarefaction was is determined only by the compressibility of the material:

$$c_0 = \sqrt{\frac{K}{\varrho}} = \sqrt{\frac{V}{\varkappa}}. \tag{11.62}$$

Speed c_l is sometimes called the speed of elastic waves, and speed c_0, the speed of plastic waves; c_0 is always less than c_l; for instance, in iron $c_l = 6.8$ km/sec and $c_0 = 5.7$ km/sec. The speed of propagation of strong compressional waves (shock waves) depends on the amplitude of the wave. It is always greater than c_0 or close to this magnitude. The speed of propagation of weak perturbations is always equal to c_l, independent of amplitude, inasmuch as perturbations spread with this speed only when they are small.

Questions of propagation of waves of rarefaction and compression in an elasto-plastic medium with a nonlinear dependence between stress and strain, similar to the dependence $\sigma_{zz}(\Delta L/L)$, which is shown in Fig. 11.34, was investigated in detail by Kh. A. Rakhmatullin. References to original works in this area may be found in the survey by Kh. A. Rakhmatullin and G. S. Shapiro [29].

In following paragraph we shall consider a simple case of propagation of waves with the shown properties of substance.

§ 17. Splitting of Compressional and Unloading Waves

Let us see what partically occurs, if to the surface of a flat body at the initial moment we apply constant pressure p. Let us consider pressure to be sufficiently small so that strain linearly depends on pressure, i.e., follows Hooke's law. Let us depict the diagram of p and V for the state of a compressed substance behind the front of a wave. Considering the "anisotropy" of pressure in the case of weak strains, instead of pressure we will operate with the normal component of stress, which affects the area parallel to the surface of the front of the wave, σ_{zz}, if the wave spreads along axis z. Along the axis of abscissas we will plot the specific volume of the body. During small strains and pressures the state is described by Hooke's law in the form of (11.55), which according to definition (11.61), can be rewritten in the form

$$\sigma_{zz} = \frac{\Delta V}{V} \rho c_l^2, \quad \sigma_{zz} < p_{кр}.$$

When pressure exceeds critical p_{crit}, and change of volume exceeds $\Delta V_{crit}/V = p_{crit}/\rho c_l^2$, the body becomes fluid and the slope of line $\sigma_{zz}(\Delta V)$ changes. By formulas (11.57) and (11.62) we have in this region

$$\sigma_{zz} = \frac{\Delta V}{V} \rho c_0^2 + \text{const}, \quad \sigma_{zz} > p_{кр}.$$

The diagram of σ_{zz} and V is depicted in Fig. 11.36.

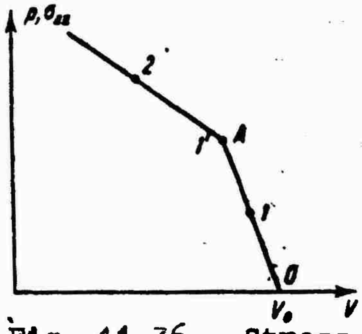

Fig. 11.36. Stress (pressure)-volume diagram (explanation in text).

If external pressure $p < p_{crit}$, through the body there will run one "elastic" compressional wave with speed c_l (Fig. 11.37a; state 1 on diagram σ_{zz} and V, Fig. 11.36). If, however, the applied pressure $p > p_{crit}$, then in the body there finally is attained state 2 on diagram σ_{zz} and V. However, in this case through the body there runs no longer one, but two waves: "elastic" with amplitude p_{crit} and the state behind the front 1', and after it "plastic" with state behind front 2 (see Fig. 11.37b). Inasmuch as $c_0 < c_l$, the plastic wave does not overtake the elastic, so that the combination of the two waves is stable.* The plastic wave runs through the slightly compressed substance, which moves with speed $u_{crit} = \frac{p_{crit}}{\rho c_l}$. This speed is extremely low; for instances, in iron the compression in the elastic wave is equal to $\frac{\Delta V_{crit}}{V} = 5 \cdot 10^{-4}$, and speed $u_{crit} = 3.6$ m/sec. Mass speed in the plastic wave is equal to $u' = \frac{p - p_{crit}}{\rho c_0}$ with respect to the substance moving in the elastic wave, and $u' + u_{crit}$ – with respect to an undisturbed substance.

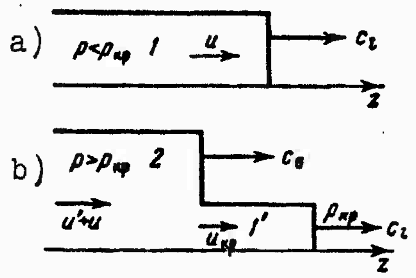

Fig. 11.37. Two cases of propagation of an acoustic wave of compression: a) one elastic wave; b) system of plastic and elastic waves.

If we consider a compressional wave of great amplitude, and all the more so shock waves with pressures of hundreds of thousand atmospheres and above, the effects of preliminary compression of the substance by an elastic wave to one or two thousand atmospheres and acceleration of it to a speed of the order of several meters per second may be disregared, considering that a plastic wave spreads through a motionless undisturbed substance with a speed corresponding to compressibility c_0.

Shock waves of sufficiently great amplitude spread with a speed noticeably exceeding c_0. If the speed of the shock wave $D > c_l$, splitting of waves in general does not occur: the shock wave as if from the very beginning runs faster than the elastic wave and is unified with it into one wave.

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*The effect of the existence of a combination of elastic and plastic compressional waves was noted by Bancroft [30] and others, devoted to phase transition in iron (see § 19).

Splitting of waves into elastic and plastic also occurs in the case of sufficiently strong unloading of a preliminarily compressed substance. Let us assume that the substance is unloaded from pressure p_0, to pressure p (for instance, at first through the body by means of its compression by a piston a compressional wave was triggered with pressure p_0, and then after a certain time the pressure on the piston drops to magnitude p). If $p_0 - p < p_{crit}$ through the compressed substance there runs one elastic wave of unloading with speed c_l. If, however, $p_0 - p > p_{crit}$ an elastic wave of unloading runs ahead, in which pressure drops from p_0 to $p_0 - p_{crit}$, and after it with smaller speed spreads a plastic wave of unloading, in which pressure drops to magnitude p, equal to pressure on the "piston" (in particular, if the piston in general is "retracted," p can be equal to zero). These two cases are shown in Fig. 11.38.

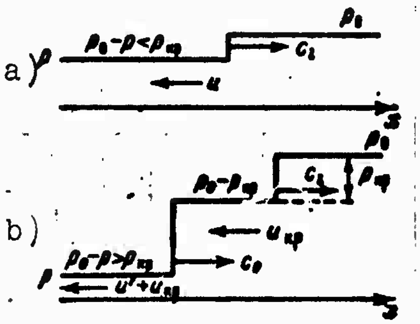

Fig. 11.38. Two cases of propagation of an unloading acoustic wave: a) one elastic wave; b) system of plastic and elastic waves.

The phenomenon of splitting of a wave of unloading into two waves was observed experimentally in [4] which will be described in the following paragraph. The authors of this work gave the observed phenomena the above-described explanation.

§ 18. Measurement of Speed of Sound in a Substance Compressed by a Shock Wave

Of great interest is the experimental determination of speed of sound behind the front of a shock wave. With this speed are propagated the disturbances overtaking the shock wave and affecting its amplitude.* The speed of sound (or adiabatic compressibility) determines the slope of the usual adiabat on diagram p, V, which passes through the point describing the state behind the front of the shock wave, i.e., it is determined by the initial behavior of the compressed substance during unloading and its behavior in a weak secondary shock wave. A knowledge of the speed of sound is important for the establishment of the equation of state of the substance and for correct formulation of experiments on shock compression. Finally, the values of the speed of sound in solid matter at high pressures are also of interest for a number of problems of geophysics.

The method of measurement of the speed of sound behind the front of a shock wave was developed by L. V. Al'tshuler and S. V. Kormer jointly with M. P. Speranskaya, L. A. Vladimirov, A. I. Funtikov, and M. I. Brazhnik [4]. One of the methods (the method of lateral unloading) consists of the following. Shock compression is applied to a cylindrical sample of stepped form (Fig. 11.39). After passage of angle O by the front of the wave, lateral unloading begins. Perturbations from unloading overtake the front and weaken the shock wave. On the weakened peripheral section of the surface of the front, the speed of the front decreases and the surfaces is distorted, as shown in Fig. 11.39; the central section of the surface, up to which the perturbations to a given moment of time still did not succeed in overtaking, remains flat, and the speed of the shock wave on it is as before. The point where weakening of the shock wave begins is easy to find from simple geometric considerations. In time t from moment of passage of angle O

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*Let us recall that a shock wave spreads through a substance behind its front with subsonic speed.

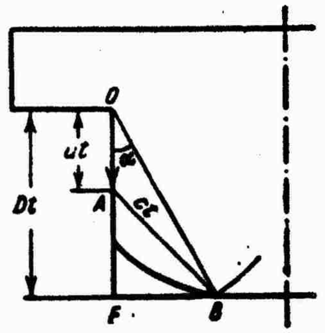


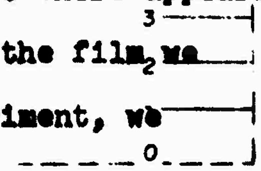
Fig. 11.39. Geometric construction in an experiment with lateral unloading.

by the front, the front departs to distance Dt. The substance, earlier located near the angle, drifts forward to distance ut, and the earliest perturbations, which were produced at the time of passage of the angle and which spread through the substance with the speed of sound c, to this moment reach a sphere of radius ct, described from point A, so that weakening of the shock wave starts at point B (see Fig. 11.39). Considering triangles OBF and ABF, it is possible to connect the speed of sound with speeds D, u and the tangent of "angle of unloading" α:

$$c=D\sqrt{(\mathrm{tg}\,\alpha)^2+\left[\left(\frac{D-u}{D}\right)/D\right]^2}.$$

The problem reduces to the determination of speed of front D and angle α (shock adiabat of substance is assumed to be known, so that mass speed u may be calculated). Experimentally, it is solved thus. Upon emergence of shock wave on free surface, the latter flies forward with a defined speed. On the central (nonweakened) section of surface of the front this speed everywhere is identical, and on the peripheral (weakened) Section it is less, as shown by the arrows in Fig. 11.40.

In the experiment we record the moments of arrival of the free surface to plexiglas plate P (by photographic means with time scanning). On the film there is obtained the picture depicted in Fig. 11.40 (at the time of impact of the substance against the plexiglas there appears an illumination which puts the curve on film). Through the film we determine point B and, knowing the geometry of the experiment, we



know the angle of unloading α.

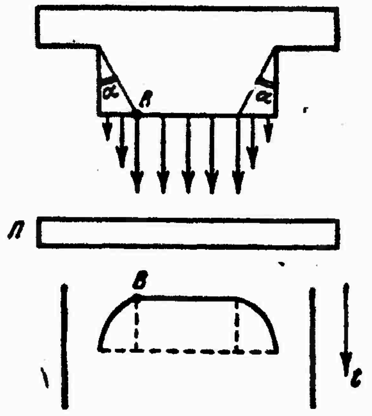


Fig. 11.40. Diagram of an experiment with lateral unloading.

It turned out that for water the boundary of the weakened and undisturbed regions of surface of the front is sharp and the modulus of compression $\rho_0 c^2$, calculated with respect to the speed of sound c, is less than the slope of shock adiabat $\rho_0 \frac{dp}{d\rho}$ (in variables p, ρ/ρ_0) at the point corresponding to the state behind the front, which is in full consent with the mutual location of shock adiabat and isentrope, shown in Fig. 11.41.

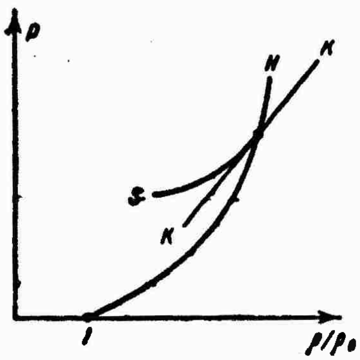


Fig. 11.41. Pressure — density diagram. H — shock adiabat. S — isentrope of unloading: KK — tangent to isentrope at the point corresponding to the state in the shock wave.

For metals (iron and copper) the curves on the film have a rounded form without a clearly expressed boundary, as if the peripheral sections of the surface of the front were unloaded strongly, and closer to the center (to the axis of the sample), very weakly.

Modulus of compression $\rho_0 c^2$, calculated by the point of origin of weak distortion of surface of the front, turned out to be greater than the coresponding slope of shock adiabat $\rho_0 dp/d\rho$ by approximately 1.5 times. Experimental data are given in Table 11.3, taken from [4].

This phenomenon was explained by the authors on the basis of presentations about the existence of two speeds of sound in a solid, which was mentioned in § 15 and 16. Weak perturbations of

Table 11.3.

Substance	α, deg	D, km/sec	u, km/cm.	Elastic c_l, km/sec	Elastic $\rho_0 c_l^2$, 10^{10} bar	$\rho_0 \frac{dp}{d\rho}$, 10^{10} bar	Plastic $\rho_0 c_0^2$, 10^{10} bar
Water	47,5	4,42	1,52	5,6	31,4	34,2	
Copper . . .	41,0	5,24	0,87	6,33	357,5	288,5	240
Iron . .	46,5	5,34	0,96	7,15	401,3	296,2	240

rarefaction spread through a compressed substance with the speed of elastic waves c_l (in a substance compressed by a strong shock wave, the pressure is "isotropic"). This increased "elastic" speed of sound also corresponds to the beginning of weak distortion of surface of the front; the modulus of compression $\rho_0 c_l^2$ corresponding to it turns out to be too large, larger than the slope of shock adiabat $\rho_0 \frac{dp}{d\rho}$, since the speed of the shock wave corresponds to the smaller, "plastic" speed of sound. Through the somewhat unloaded substance there runs a "plastic" wave with decreased "plastic" speed of sound. With this speed there spread considerable perturbations, rendering an essential weakening influence on the front of the shock wave. The speed of a plastic wave is determined only by compressibility and namely with it there should be compared the slope of shock adiabat. Modulus of compression $\rho_0 c_0^2$, calculated with "plastic" speed of sound c_0, turns out to be for metals, as also for water, less than slope $\rho_0 \frac{dp}{d\rho}$, in full conformity with the theory of shock adiabat (water, as a liquid, possesses only one, plastic, speed of sound c_0). The existence of two speeds of sound strongly hampers the exact determination of the boundary of "plastic" unloading, which also presents basic interest since it namely determines the compressibility of the substance. In order to be free from the influence of this effect, the authors of [4] developed another method (method of overtaking unloading, which in its initial form was offered by Ye. I. Zababakhin. This method considers the collision of a dispersed plate and sample made from the same investigated material with known shock adiabat. The x and t-diagram of the process is shown in Fig. 11.42.

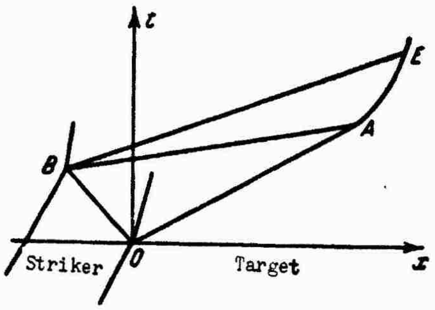


Fig. 11.42. x, t-diagram for experiment with overtaking unloading.

From the point of collision O through both bodies there spread shock waves OA and OB. After the shock wave in the striker reaches free boundary B, the unloading begins there, and the wave of rarefaction runs through the substance, overtaking the front of the shock wave in the sample at point A. From this moment the amplitude of the shock wave is weakened and the trajectory of the front bends, as shown in Fig. 11.42.

Determining, in an experiment, the trajectory of the front of a shock wave in the stage of noticeable weakening AE and considering the process of propagation of rarefaction perturbations, we can find the speed of sound in the compressed substance behind the front. Inasmuch as we are considering a stage of strong weakening of a shock wave, which is only the result of a plastic wave, but not an elastic one, carrying weak perturbation, the speed of sound determined in the experiment is a "plastic" speed, connected with the compressibility of the substance (details of this method see [4]).

For an illustration of the numerical values in Table 11.4 we shall present certain results of measurements. For comparison in the same place there are shown the speeds of sound (plastic)c_0 at normal conditions.

Table 11.4. Speeds of Sound at High Pressures Measured in Experiment

Metal	p, 10^{10} bar	V_0/V	c_s, km/sec	c_0, km/sec (at normal conditions)
Al	195,5 160,0	1,76 1,701	11,74 11,23	5,2
Cu	279,6 211,7	1,694 1,636	9,48 8,93	3,9
Fe	347,8 284,9	1,650 1,600	9,48 9,53	5,7

§ 19. Phase Transitions and Splitting of Shock Waves

Many solids can, under various conditions, remain in different crystal modifications. At certain values of temperatures and pressures, connected by a determined dependence, there are possible transitions from one modification to another. These transitions are accompanied by change of volume and liberation (or absorption) of latent heat, which is in first-order phase transitions. Similar transitions are frequently called polymorphous transformations of a substance.*

An example of a substance that is able to experience a polymorphous transformation is iron. At atmospheric pressure and temperature 910° C iron is transformed from α-phase into γ-phase; transition is accompanied by a 2.5% decrease in volume and absorption of latent heat 203 cal mole. Polymorphous transformations frequently occur at high pressures. In particular, the shown transition in iron, at a temperature slightly exceeding normal, occurs at a pressure of 130,000 atm.

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*In waves of sufficiently large amplitude there occurs melting of the solid substance, which also is a first order phase transition. Problems of melting in shock waves presently are not being studied experimentally nor theoretically.

Unique phenomena appear during shock compression of a substance that is able to experience polymorphous transformations at high pressures. These phenomena were considered theoretically (mainly qualitatively) by Bancroft, Peterson, and Minshall [30], Duff and Minshall [31], and Drummond [32]. Experimentally, shock waves in the presence of polymorphous transformations were studied in the first two works (in the first — in iron, in the second — in bismuth); in the works of A. N. Dremin and G. A. Adadurov [33] (marble), and A. N. Dremin [34] (paraffin).

In a certain range of pressures through a body that is able to experience polymorphous transformations, there spread not one, but two shock waves, following one after the other. Such shock wave splitting is connected with the anomalous behavior of the shock adiabat of the substance in the region of phase transition. At not too large pressures in the shock wave there occurs an insignificant increase of entropy; therefore, the shock adiabat is close to the isentrope and in examining the shown phenomenon it is possible to originate from the usual adiabat.

The adiabat of a substance experiencing polymorphous transformation is schematically depicted in Fig. 11.43.

During compression from normal volume until achievement of a certain state A there starts a transition from phase I to phase II. The crystal lattice is reconstructed in such a way that the new equilibrium positions of atoms correspond to the smaller interatomic distances; therefore, reduction of volume in the region of transition requires a much smaller increase of pressure than in initial phase I (at absolute zero temperature the phase transition I-II occurs at constant pressure and section AB of the adiabat $S = 0$ — this is a straight horizontal line, as shown in Fig. 11.43b). If there was no

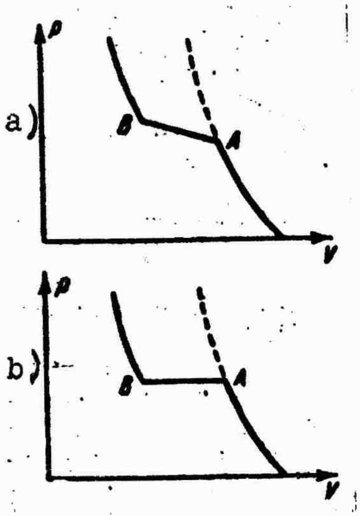

Fig. 11.43. Isentrope (usual adiabat) of a substance experiencing polymorphous transformation: a) at temperature T > 0 different from zero; b) at absolute zero T = 0.

reconstruction, the pressure curve would continue from point A upwards as shown in Fig. 11.43 by the dotted line. In region AB the substance is in a two-phase state. Full reconstruction of the lattice and full transformation of the substance from phase I into phase II terminates at moment B, after which the adiabat of the second phase again steeply goes upwards. Compressibility of a substance in various phase are different, so that the slopes of curves corresponding to single-phase state in points A and B in general are different.

Let us now imagine a body that has a shock adiabat of the described type, and let us assume that in the initial moment to its surface there is applied a constant pressure p (we shall consider a one-dimensional plane case). We shall consider that this pressure is sufficiently great so that it is possible to disregard the effects of strength and consider the pressure to be hydrostatic, i.e., we shall disregard the possible existence of an "elastic " wave (see § 17), considering that the shock wave is "plastic."

If pressure p is lower than pressure p_A, at which the phase transition begins, through the body there runs the usual shock wave, the state of the substance in which corresponds to the point lying on the shock adiabat (point C in Fig. 11.44); the speed of propagation of shock wave D is determined, as it is known, by the slope drawn from the point of initial state O to the point of final state on the shock adiabat,

$$D = V_0 \sqrt{\frac{p - p_0}{V_0 - V}}.$$

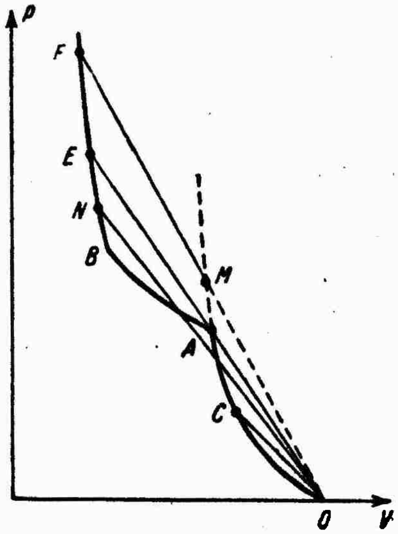

Fig. 11.44. pV diagram illustrating different cases of propagation of a shock wave during polymorphous transformation of a substance (explanation in text).

If pressure p is greater than magnitude p_E, which corresponds to line OE touching the shock adiabat in intermediate point A, for instnace, equal to p_F, than through the body there also runs one shock wave, behind the front of which there is attained state F. However, in this case the substance behind the front is in another phase, i.e., II. Transition from phase I to phase II occurs in the front of the shock wave. Usually the phase transition requires much more time than necessary for establishment of thermodynamic equilibrium in an ordinary single-phase substance. The situation in this case in many respects is analogous to that which takes place in a shock wave that is spreading through a gas with retarded excitation of certain degrees of freedom (for instance, through a dissociating gas). Direct shock compression leads to intermediate state M, which lies on the extrapolated shock adiabat of phase I, responding to the absence of phase transition (this corresponds to the viscous shock in a gas). Then the phase transition begins and the width of the front is determined by the relaxation time of the transition, just as the width of the front of a shock wave in a gas is determined by the dissociation time. The profile of pressure in a shock wave has the form depicted in Fig. 11.45, and is completely analogous to the profile of pressure in a dissociating gas. The point describing the state in the expanded zone of the front of a wave then passes through a segment of line MF in Fig. 11.44.

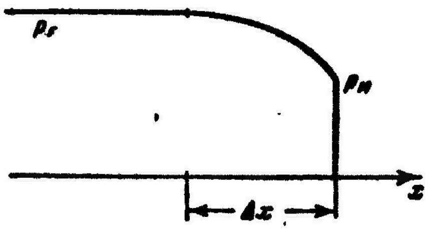

Fig. 11.45. Profile of pressure in a shock wave with "relaxation" of phase transition.

Let us now consider an intermediate case when the pressure applied to the body is between p_A and p_E, let us say, and is equal to p_N (point N on shock adiabat, Fig. 11.44).

Speed of a shock wave, determined by the slope of line ON, is now less than the speed of a shock wave of smaller pressure P_A, corresponding to point A, which is determined by the slope of steeper line OA. Therefore, a wave with pressure p_A overtakes a shock wave with pressure p_N. (Let us note that line ON three times intersects the shock adiabat, i.e., to the same wave speed correspond the three values of pressure and volume. It is clear that such ambiguity is physically unreal.)

At intermediate value of pressure $p_E > p > p_A$ there occurs splitting of the shock wave into two independent waves, which follow one after the other (this case is specially shown in Fig. 11.46). In the first shock wave the substance is compressed from initial state 0 to state A, corresponding to the beginning of phase transition, where the speed of propagation of the first shock wave through an undisturbed substance is determined by the slope of line OA in accordance with the formula:

$$D_1 = V_0 \sqrt{\frac{p_A - p_0}{V_0 - V_A}}.$$

Behind the first wave there follows a second shock wave, in which the substance is compressed from state A to final state N. Speed of propagation of this second wave through a compressed and moving substance, remaining in state A, is determined by the slope of line AN and is equal to

$$D_2 = V_A \sqrt{\frac{p_N - p_A}{V_A - V_N}}.$$

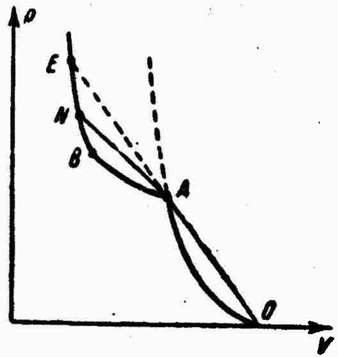

Fig. 11.46. pV diagram illustrating the splitting of a shock wave.

Speed of propagation of the second shock wave with respect to a motionless parent substance is equal to the sum of speed D_2 and mass speed of the substance in the first shock wave u_A:

$$D_2' = D_2 + u_A.$$

It is easy to see that the second wave does not overtake the first, i.e., the combination of the two shock waves is stable. Actually, the speed of propagation of the first wave with respect to the substance behind it is equal to

$$D_1'' = V_A \sqrt{\frac{p_A - p_0}{V_0 - V_A}}.$$

Inasmuch as the slope of line OA by definition ($p_N < p_E$) is greater than the slope of line AN, we have $(p_A - p_0)/(V_0 - V_A) >$ $> (p_N - p_A)/(V_A - V_N), D_1'' > D_2$, i.e., the first wave runs through the substance faster than the second with respect to the very same substance.

In the front of the second shock wave there occurs a phase transition: in initial state A the substance is in the first phase, and in final N it is either in the second, if $p_N > p_B$, or in a two-phase state, if $p_N < p_B$ (transition in this last case is incomplete). By virtue of deceleration of phase transition the front of the second shock wave turns out to be strongly eroded, in distinction from the thin front of the first wave. The profile of pressure in the case of a system of two waves is schematically depicted in Fig. 11.47. With the passage of time the distance between fronts of both waves is increased, inasmuch as their speeds are different; distribution of pressure in the second wave is stationary, and the profile in the

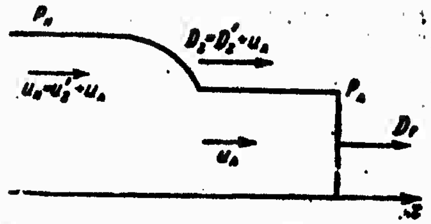

Fig. 11.47. Profile of pressure in the case of splitting a shock wave into two parts.

second wave is propagated as a whole.

The combination of two shock waves in the presence of phase transition in many respects is analogous to the combination of two compressional waves: "elastic" and "plastic," which was considered in § 17. The cause of the appearance of two waves in both cases is the anomalous behavior of the adiabat and shock adiabat, at which there exists a region on the adiabat where the latter is turned with convexity upwards.

In Chapter I it was shown that on the sign of the second derivative $\partial^2 p/\partial V^2$ depends whether entropy increases or decreases in the shock wave, i.e., the sign stipulates purely thermodynamic conclusions. Here we are convinced in the fact that the anomalous behavior of the shock adiabat leads to anomalous kinematic consequences, i.e., splitting of the shock wave in two. The limiting condition $p > p_E$ for unification of two waves into one corresponds to the position in the case of combination of shock and plastic waves, when the speed of the plastic wave, due to deviation of the adiabat from Hooke's law, becomes greater than the speed of the elastic wave, so that the second wave overtakes the first and merges with it.

As was already mentioned above, the phenomenon of splitting of a shock wave in substances experiencing polymorphous transformations, was observed experimentally. For an illustration, Fig. 11.48 shows the shock adiabat of iron in the region of phase transition, found experimentally in [30]. Let us note that in bismuth the phase transition occurs at a pressure of ~28,500 atm, where by the relaxation time for the transition at 42°C turned out to be less than 1 millisecond.

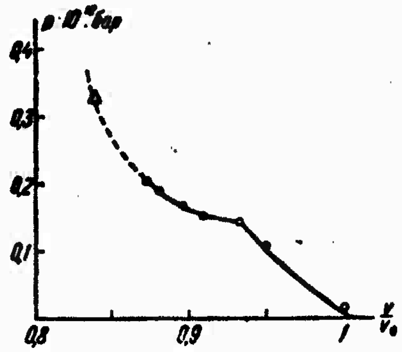

Fig. 11.48. Shock adiabat of iron in the region of phase transition. Δ — according to [24], o — according to [30].

Alder and Christian [35] revealed a phase transition of the first kind in iodine J_2 (crystals of iodine are molecular) at a pressure of $p \approx 7 \cdot 10^5$ atm and relative volume $V/V_0 \approx 0.53$. Transition was fixed by changing the slope in the linear dependence of speed of the front of the shock wave on mass speed. Calculations show that temperature in the wave at the point of phase transition $T \approx 1$ ev. It is comparable with the dissociation energy of iodine molecules 1.53 ev. It is assumed that phase transition is connected with transformation of a molecular diatomic crystal into a monatomic metallic state.

It is interesting that the anomalies in the curve of cold compression of metals, and consequently also in the shock adiabat, similar to the ones that appear in the presence of polymorphous transformations, can also appear in the absence of reconstruction of the atomic lattice due to change of structure of electron zones and the covering of separate zones during compression. The possibility of change of properties of metals upon change of zonal structure is noted by I. M. Lifshits [36]. The influence of these changes on the curve of cold compression of metals and the appearance of sections of anomalous behavior of the curve, where $\partial^2 p/\partial V^2 < 0$, was studied by G. M. Gandel'man [37].

§ 20. Shock Wave of Rarefaction in a Medium Experiencing Phase Transition

According to the general theory presented in § 17, 18 and 19, Chapter I, during anomalous adiabatic behavior, when there are sections where the adiabat is turned with its convexity upwards ($\partial^2p/\partial V^2 < 0$), there is the possible appearance of rarefaction shocks. The adiabat of a solid which is experiencing phase transition exactly gives such a possiblility. This was noted in [32]. Regimes with shock waves of rarefaction in a metal in the presence of phase transformations were studied by A. G. Ivanov, S. A. Novikov, and Yu. P. Tarasov [38], who were the first to give clear experimental proof of the existence of rarefaction shocks in iron (steel).

On the adiabat of a substance which is experiencing polymorphous transformation, in the region of the point of break A (Fig. 11.43) the movement of the adiabat is anomalous. Although in all points where the adiabat does not have peculiarities, the second derivative $\partial^2p/\partial V^2$ is positive, nonetheless there is a section in the region of point A where the chord connecting any two points 1 and 2, wholly lies below the adiabat (Fig. 11.49). This is the consequence of negativity of the mean value of the second derivative on § 1-2:

$$\left\langle \frac{\partial^2 p}{\partial V^2} \right\rangle_{12} = \left[\left(\frac{\partial p}{\partial V} \right)_2 - \left(\frac{\partial p}{\partial V} \right)_1 \right] / (V_2 - V_1) < 0 \text{*)}.$$

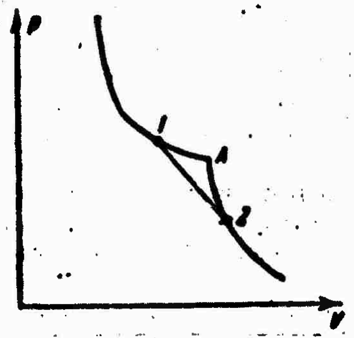

Fig. 11.49. Anomalous section of adiabat.

As it is known from the general theory, namely such a position also leads to anomalies in hydrodynamic regularities.

Propagation of shock waves of compression in a similar substance was considered in the preceding paragraph.

Let us now consider the unloading of substance that is preliminarily compressed by a shock wave. Let us assume that at the time t = 0 in a body that has

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*In all points of § 1-2, besides point of break A, $\partial^2p/\partial V^2 > 0$, but in point A itself, $\partial^2p/\partial V^2 = -\infty$, so that the mean value on § 1-2 is negative all the same.

earlier been compressed by a shock wave to state 1 (p_1, V_1), there is a region of rarefaction in which pressure and volume change smoothly to the values of p_2, V_2 (state 2; $p_2 < p_1$, $V_2 > V_1$). Initial distribution of pressure with respect to coordinate is shown in Fig. 11.50. We assume that the points of initial and final states 1 and 2, and also all intermediate points in smooth distribution lie on the isentrope and the process is adiabatic.* Some of the corresponding points are designated in Fig. 11.50 and in the adiabate in Fig. 11.51 by identical letters and figures.

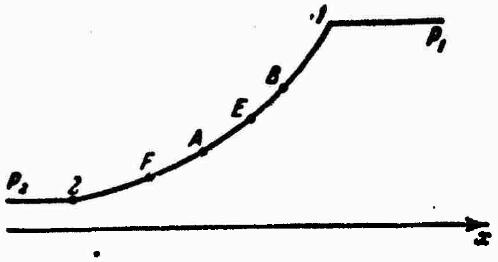

Fig. 11.50. Concerning the question on evolution of a region of rarefaction; initial profile of pressure.

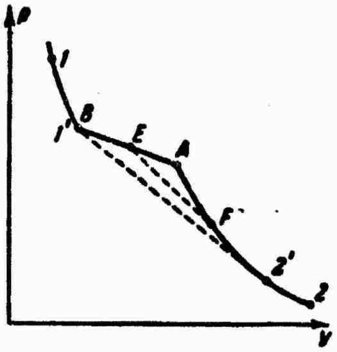

Fig. 11.51. Concerning the question on evolution of a region of rarefaction; states on p, V diagram corresponding to the profile depicted in Fig. 11.50.

Let us consider a simple rarefaction wave (see § 8, Chapter I), spreading to the right through a compressed substance. In order for the wave to be simple, it is necessary that the initial distributions of pressure and speed with respect to coordinate p(x, 0), u(x, 0) satisfy the condition of constancy of Riemann invariant $J_-(x, 0)$ = const. Then, and in subsequent moments of time, $J_-(x, t)$ = const. We shall assume that this condition is carried out. As it is known (see § 8, Chapter I), in a simple wave, spreading to the right, the

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*We consider only small pressures at which the thermal effects are small and the shock adiabat practically coincides with the isentrope. Furthermore, we consider that phase transitions occur sufficiently fast "instantly", so that the states of the substance never deviate from the thermodynamically equilibrium adiabat.

C_+-characteristics are lines on plane x, t; along them are plotted the constant values of pressure and other magnitudes.

Let us consider what will occur with our initial profile of pressure in subsequent moments of time. For this, on plane x, t in Fig. 11.52 we shall plot the C_+-characteristics: straight lines with slopes $\frac{dx}{dt} = u + c$. The speeds of propagation of perturbations ("speeds of sound") in different points of initial distribution are determined by the slopes of tangents to the adiabat in corresponding points. In two points of break A and B the speed of sound experiences a jump (dependence of speed of sound on volume is shown in Fig. 11.53). Speed of the substance, equal by virtue of condition $J_- = \text{const}$, $u = -\int c \frac{d\rho}{\rho} + \text{const}$, is continuous in points A and B, so that the slopes of the characteristics intermittently change together with jumps of the speed of sound.

Fig. 11.52. x, t, diagram illustrating the evolution of initial rarefaction in a substance with anomalous adiabat.

From the "normal" point of break B there emerge two C_+-characteristics with different slopes having identical values of pressure, but different values of speed of sound. These speeds of sound correspond to the values on both sides of the break on the adiabat, whereby slightly the larger value of pressure $p_B + \varepsilon$ (ε is infinitesimal) spreads faster than the slightly smaller $p_B - \varepsilon$.

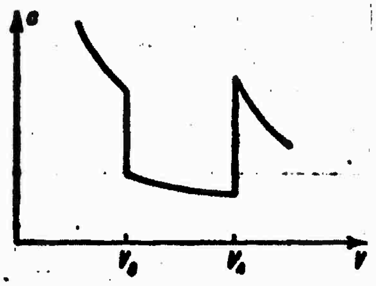

Fig. 11.53. Dependence of speed of sound on volume, corresponding to the adiabat depicted in Fig. 11.51.

Another position is in the "anomalous" point of break A. Here from point A there also emerge immediately two characteristics, but the ~~greater the pressure $p_A + \varepsilon$ spreads~~

STOP HERE

slower, the smaller $p_A - \varepsilon$. The characteristics drawn from points adjacent to A tend to intersect (see Fig. 11.52), and the limiting characteristics, emerging from point A itself, as if was intersected already from the very beginning. This means that in the initial distribution of pressure at point A from the very beginning there will form a little break (in limit $t \to 0$ it is infinitesimal), which grows with the passage of time.*

Propagation of the rarefaction wave and pressure profile in consecutive moments of time are depicted schematically in Fig. 11.54. The "plateau" pressure p_B is "limited" by the characteristics emerging from point B in Fig. 11.52.

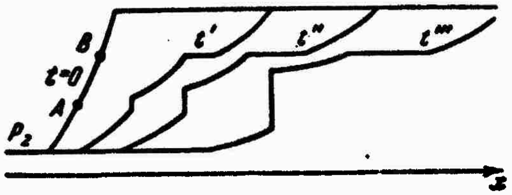

Fig. 11.54. Evolution of pressure profile in a rarefaction wave; formation of a shock wave of rarefaction. t = 0, t', t", t"' – consecutive moments of time.

The jump — a shock wave of rarefaction appearing at point A — grows in accordance with the intersection of characteristics. The jump grows, i.e., the upper, initial, pressure is increased, and the lower, final, drops as long as the peak of the jump runs through the substance in front of the jump with supersonic speed, and the lower one runs through the substance behind the jump with subsonic speed. The upper boundary of the jump as if "consumes" sections of the smooth increasing distribution of pressure, and perturbations of rarefaction from below behind the jump overtake the jump, strengthening

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*The situation in the smooth origin of a compressional wave with normal properties is somewhat different. The characteristic curves in this case do not immediately intersect (see § 9 and 12, Chapter 1), the curvature of the pressure profile gradually increases, and the discontinuity — the shock wave — is not immediately formed. Here the discontinuity — a rarefaction shock wave — originates from the very beginning, and the amplitude of its growth is proportional to time.

the discontinuity. The process of growth of the jump stops when the upper pressure attains the pressure in the plateau, and the speed of propagation of the lower boundary through the substance behind the jump becomes sonic.

The steady-state position of discontinuity (points 1'-2' on the adiabat, Fig. 11.51) and the pressure profile in a rarefaction wave are shown in Fig. 11.55. As we know (see § 14, Chapter I), the speeds of propagation of discontinuity 1'-2' through the substance in front of it u_1 and through the substance behind it u_2 are determined by the slope of line 1'-2':

$$u_1^2 = V_{1'}^2 \frac{p_{1'}-p_{2'}}{V_{2'}-V_{1'}}, \quad u_2^2 = V_{2'}^2 \frac{p_{1'}-p_{2'}}{V_{2'}-V_{1'}}.^*$$

From Fig. 11.51 it is clear that point 2' is determined by the condition of contact of line 1'-2' with the adiabat, since with this $u_2 = c_{2'}$. The speed of propagation of a discontinuity through the substance in front of it u_1 is less than the upper speed of sound at the point of discontinuity B, but greater than the lower speed: line 1'-2' is more sloping and steeper than the corresponding tangents to the adiabat at point B.

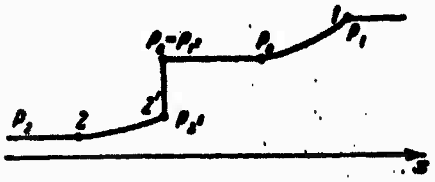

Fig. 11.55. Character of final distribution of pressure in a wave of rarefaction. Distribution extends with the passage of time, not changing its form.

In practice, a wave of rarefaction usually appears when a shock wave emerges on the free surface of a body. The regime is then self-similar, all C_+-characteristics on plane x and t emerge from one point

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*These formulas follow from the laws of conservation of mass and momentum in a discontinuity and are equally valid both for jumps of compression and also for jumps of rarefaction.

and the whole "steady-state" pressure profile, depicted in Fig. 11.55, will form from the very beginning, as in the usual self-similar wave of rarefaction (see § 11, Chapter I). Thus, the wave of rarefaction has a complicated profile consisting of two sections of smooth lowering of pressure, a plateau of pressure (all three of these sections extend with the passage time in accordance with the self-similarity of the regime) and the jump of the shock wave of rarefaction (if the surface of the body is free, point 2 of final state corresponds to zero pressure). The x, t-diagram for a centered wave of rarefaction is shown in Fig. 11.56.

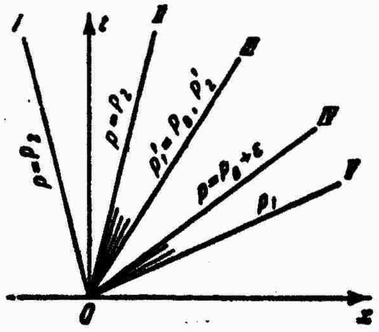

Fig. 11.56. x, t-diagram for a self-similar rarefaction wave formed upon emergence of a shock wave on the surface. I — line of free surface, II — tail of rarefaction wave, III — line of rarefaction wave, IV — beginning of plateau of pressure, V -- head of rarefaction wave.

In experiments described in [38], there were revealed unusual break-away phenomena during blasting of explosive charges on the surface of iron and steel samples. The break-away surface was extraordinarily smooth. This phenomenon was interpreted as the result of the collision of two shock waves of rarefaction, when on a certain surface there appears an intermittent change of pressure from positive to negative values. Usually during smooth unloading the zone of tensile stresses provoking the break-away is blurred, and the break-away surface is rough, which is connected with the microheterogeneity of the material in the extended zone of tensile stresses. Analysis of the complicated picture of motion under the conditions of the experiment allowed the authors of [38] to conclude that the observed phenomena are connected with the existence of shock waves of rarefaction. Another confirmation is the circumstance that in other materials, besides iron and steel, in which there are no phase transitions in the investigated region of pressures, there were no unusual splittings.

4. Phenomena Upon Emergence of a Powerful Shock Wave on the Free Surface of a Body

§ 21. Limiting Cases of Solid and Gaseous States of an Unloaded Substance

Section 11 considered the process of unloading of a solid that was initially compressed by a shock wave, after the wave emerges on the free surface. It was considered that the shock wave is not very strong, the temperature behind the front is comparatively small and, unloaded to zero pressure, the substance remains solid.

It is clear that if a shock wave is very powerful and the internal energy of the heated substance ε_1 many times exceeds the binding energy of atoms U (equal to the heat of evaporation at zero temperature), then upon expansion of the substance to a low (zero) pressure after the emergence of the shock wave on the free surface, the substance is completely evaporated and behaves as a gas during unloading.* In particular, during unloading in a vacuum, i.e., to strictly zero

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*Sometimes we speak of the "evaporation" of a substance in the shock wave itself. Such an affirmation is incorrect, if by "evaporation" we understand a phase transition in the usual thermodynamic meaning. To call a solid substance a "liquid" or "gas" is possible only in a conditional sense, depending upon the relationship between kinetic energy of thermal motion of atoms and the potential energy of their interaction. Transition from "liquid" to "gas," if one heats the substance at constant volume, is carried out continuously. In general, it is necessary to remember that at pressures and temperatures higher than critical, the entire substance is uniform and separation of phases does not occur. It is necessary to note that the affirmation about the fact that in a sufficiently strong shock wave the substance ceases to be solid, has a fully real physical meaning (solid matter melts).

pressure, the density and temperature on the front edge of the substance are also equal to zero.

Distributions of density, speed, and pressure in an unloading wave have qualitatively the same character as also in a wave of rarefaction in a gas (see § 10 and 11, Chapter I). They are depicted in Fig. 11.57.

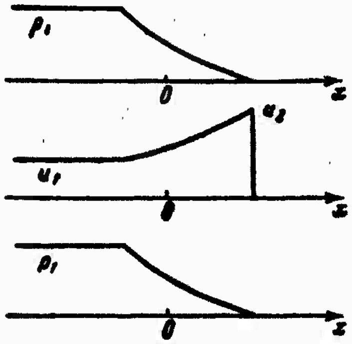

Fig. 11.57. Profiles of density, speed, and pressure after the emergence of a very strong shock wave on a free surface.

The hydrodynamic solution for a self-similar unloading wave may be written in general form independently of the thermodynamic properties of the substance. It is expressed by the formulas

$$\frac{x}{t}=u-c, \tag{11.63}$$

$$u+\int\frac{dp}{\rho c}=\text{const} \tag{11.64}$$

for a wave running to the left, as shown in Fig. 11.57.

Integration is conducted at constant entropy S, since the process of unloading is adiabatic. In this case the entropy is equal to the entropy of the substance behind the front of the shock wave. It is possible to express the constant through the parameters of the substance in the front of the shock wave (which we mark by index "1"). Formula (11.64) then obtains the form

$$u=u_1+\int_p^{p_1}\frac{dp}{\rho c}. \tag{11.65}$$

Speed of the front edge of an unloaded substance (speed of free surface) is equal to

$$u_2=u_1+\int_0^{p_1}\frac{dp}{\rho c}. \tag{11.66}$$

We have already used formula (11.66) in § 11 in order to obtain the law of doubling of speeds. Distribution of hydrodynamic magnitudes in an unloading wave can be found if we know the thermodynamic functions of the substance (i.e., functions ρ (p, S), c (p, S), are known, with the help of which it is possible to calculate the integral (11.65)). Corresponding formulas for gas with constant heat capacity were written out in § 10, Chapter I.

In the case of unloading of solids of interest to us this cannot be done, since for description of the thermodynamic functions of the substance in the region of densities somewhat less than the normal density of a solid, there is presently no satisfactory theory (consider the intermediate temperatures at which the substance can be considered neither a solid, nor an ideal gas). Therefore, here we shall limit ourselves to the description of the qualitative picture and rough estimates.

For simplicity we shall assume that until compression of the shock wave the solid was at zero temperature and zero volume V_{0K}, and also that unloading occurs in a vacuum (to zero pressure). Furthermore, we shall not make a distinction between solid and liquid state. Melting heat usually is much less than the heat of evaporation* (the change of volume during melting is also slight); therefore, considering phenomena of such energy scales in which the substance is completely evaporated, the effect of fusion may be disregarded.

Let us trace the process of unloading of a given particle of substance on a p and V-diagram. In Fig. 11.58 there are curves of elastic pressure p_x extended also to the region of negative pressures,

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*For instance, 46 times less in lead, and in aluminum, 22 times less.

shock adiabat p_H, and curve OKA dividing the region of one-phase and two-phase states. Branch OK to critical point K constitutes the boiling curve (beginning of vaporization), and branch KA is the curve of saturated vapor (beginning of condensation). Furthermore, several adiabats S are drawn, passing through different states in the shock wave.

Let us consider the simplest limiting cases. Let us assume that the wave is weak (state I on shock adiabat). The compressed substance is unloaded along adiabat S_1, pressure drops to point B_1 where the adiabat intersects the boiling curve, after which the solid (or liquid) in principle should boil. However, for the formation of nuclei of a new phase, i.e., vapor bubbles, there is required a rather considerable activation energy necessary for breaking the continuity of the substance and for forming a surface of bubbles; the speed of this process is so insignificant at low temperatures of the order of hundreds and even a thousand degrees (for metals) that the solid practically continues to expand and cool to zero pressure on the adiabat of the "overheated liquid," shown in Fig. 11.58 by the dotted line. In final state the substance has volume V_2* which somewhat exceeds zero volume V_{0K}, and turns out to be heated to temperature T_2, connected with the difference of volumes $V_2 - V_{0K}$ by the law of thermal expansion (see § 11). Even if one disregards the questions of the kinetics of volume vaporization, a fraction of evaporated substance could not exceed a magnitude of the order $c_V T_{B1}/U$, which is very small at temperatures T_{B1} of the order of hundreds of degrees (for metals $U/c_V \sim 10^4$ °K). We dealt

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*In distinction from the designations in § 11, here all magnitudes in final, unloaded state are marked by index "2", index "1" will be added to magnitudes in the shock wave front.

Fig. 11.58. Adiabats of unloading on p and V-diagram.

with this case of unloading in § 11.

In another limiting case, when the shock wave is very powerful (state 4), the adiabat of unloading S_4 passes much higher than critical point K, into a purely gas region, and the substance is expanded as a gas to infinite volume. In general, the adiabat at some moment will intersect the curve of saturated vapor (point B_4), after which condensation should begin*. However, if the time of divergence of vapor is limited, as this usually occurs in laboratory conditions, condensation practically does not occur, and the substance continues to expand with respect to the adiabat of supercooled vapor (dotted line in Fig. 11.58).

§ 22. Criterion of Full Evaporation of a Substance During Unloading

We shall establish a quantitative criterion of full evaporation of a substance during unloading which is more definite than the condition of very large excess of energy in a shock wave above the heat of evaporation $\varepsilon_1 \gg U$, which causes no doubts.

We shall speak of full evaporation, if an unloaded substance, following the laws of thermodynamics, passes through a stage of purely gaseous state (we do not affirm that the final state is also purely

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*The process of condensation during vapor expansion in a vacuum was considered in detail in Chapter VIII.

gaseous, since in principle during expansion to an infinite volume, condensation certainly should begin.

Let us consider the range of amplitudes of shock waves which is intermediate between two limiting cases, when the wave is weak and the unloaded substance is knowingly solid, and when the wave is very powerful, and substance during unloading knowingly behaves as a gas.

Internal energy of compressed substance in the shock wave consists of elastic ε_{x1} and thermal ε_{t1} (in the latter we will not distinguish atomic and electron). During expansion of the compressed substance to zero volume V_{OK}, the elastic energy earlier obtained during compression completely "comes back;" it changes into the kinetic energy of the substance accelerated during unloading*.

Part of the initial thermal energy ϵ_t, expended in the accomplishment of work of expansion and equal to $\int_{V_1}^{V_{0K}} p_T\, dV$, also changes into kinetic energy. Let us designate the thermal energy remaining in the substance to the moment of its expansion to zero volume V_{OK} through ε_t'. It coincides with the full internal energy at this instant. It is absolutely clear that for full evaporation in the process of subsequent expansion it is necessary for this energy ε_t' to exceed binding energy U:

$$\varepsilon_t' > U.$$

The whole question consists in what should this excess be. During expansion to volumes greater than zero, the reserve of energy

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*But does not remain concentrated in the very same particle like this occurs during stationary expiration, when Bernoulli's law is valid; see § 11 Chapter I.

ε_t' is expended partially for the accomplishment of work of expansion (this part of the energy changes into the kinetic energy of hydrodynamic motion), and partially for surmounting the adhesive forces described by negative pressure p_x (this part of the energy changes into potential energy).

Let us assume that energy ε_t' suffices in order to completely evaporate the substance, i.e., so that pressure $p = p_t + p_x = p_t - |p_x|$ does not drop to zero before the substance expands to infinite volume. From the adiabatic equation $d\varepsilon + p\ dV = 0$, by virtue of the determination of $d\varepsilon_x + p_x\ dV = 0$ it follows that $d\varepsilon_t + p_t\ dV = 0$. Integrating this equation from zero volume $V_{0к}$ to infinite, at which the thermal energy turns into zero, we obtain

$$\varepsilon_t' = \int_{V_{0к}}^{\infty} p\,dV + \int_{V_{0к}}^{\infty} |p_x|\,dV = \int_{V_{0к}}^{\infty} p\,dV + U.$$

The first member constitutes that part of the reserve of energy which goes for the accomplishment of work of expansion and the second is the energy expended for breaking the bonds of the atoms.

Let us depict on the diagram p, V the pressures p, p_t, p_x (see Fig. 11.59). In the same place are shown the energies numerically equal to corresponding areas.

On the limit of full evaporation the pressure in that stage of expansion when the adhesive forces weaken ($V > V_{max}$), close to zero (the thermal pressure is enough to surmount the adhesive forces: $p_t \approx |p_x|$). However, at an earlier stage, when $V_{0к} < V < V_{max}$, pressure p is great, and thermal pressure is noticeably greater than elastic $p_t > |p_x|$. This is clear from the fact that in the state with $V = V_{0к}$, $p' = p_t' = \Gamma \dfrac{\varepsilon_t}{V_{0к}} > \Gamma \dfrac{U}{V_{0к}}$, where Γ is the effective Grueneisen

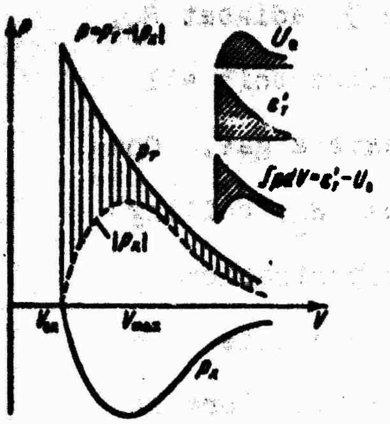

Fig. 11.59. Concerning the question about evaporation of a condensed substance during expansion (see explanation in text).

coefficient" which is of order of unity ($|p_x|$ max ~ U/V_{0K}). Thermal pressure during expansion drops more or less monotonically (energy ε_t decreases, volume V grows). Therefore curve $p_t(V)$ has exactly the form, that is depicted in Fig. 11.59. From Fig. 11.59 it is clear that the vertical shaded area, equal to the work of expansion

$$\int_{V_{0K}}^{\infty} p\,dV,$$

is of the same order as the area corresponding to potential energy U, i.e., at the limit of full evaporation the reserve of energy ε_t' should once every two times exceed binding energy U.

In order to encircle these especially qualitiative considerations in quantitative form, it is necessary to know the thermodynamic properties of the substance in the region of volumes greater than the normal volume of condensed state, when the adhesive forces are essential. Unfortunately, this range of volumes $V_{0K} < V \lesssim 5V_{0K}$ has been investigated the worst of all both theoretically and experimentally. It is possible to approach the appraisal of intensity of a shock wave, which divides the region of complete and incomplete evaporation during unloading, somewhat differently, by characterizing the boundary of full evaporation not by the magnitude of energy ε_T', but by the value of entropy.

From Fig. 11.58 it is clear that the effective boundary between complete and incomplete evaporation during adiabatic unloading is such a state in the shock wave K_H, in which entropy is equal to the entropy of the critical point S_{crit} i.e., when the expanded substance goes into critical point K. The fact that with entropy larger than S_{crit}, the substance at some moment starts to be condensed (state 3, adiabat S_3, point of condensation B_3), and this means that just before this all interatomic bonds were broken, i.e., the substance became a gas. Conversely, if entropy is less than S_{crit} (state 2, adiabat S_2, boiling point B_2), the thermal energy is not enough to bring vaporization to an end. At entropies close to critical and from either side, the substance in unloading is in a two-phase state, i.e., in the form of vapor and liquid drops. Here an essential role is played by the kinetics of phase transitions. These very interesting questions still have not been considered theoretically and have not been studied experimentally.

The entropy criterion, in spite of all its conventionality, has an advantage, as compared to the energy criterion, that permits us to approach an estimate of boundary, critical entropy S_{crit} from the "gas side" poorly passing the investigated region of volumes, two or three times exceeding the normal volume of the solid*.

In order to illustrate the presented qualitative considerations, we shall make an appraisal for lead. We shall compute the entropy of lead at the critical point, using the general formula for the entropy of a monatomic ideal gas (4.16), as are lead vapors. For the appraisal we shall use critical temperature equal to $T_{crit} = 4200^{\circ}K$, and volume $V_{crit} = 3V_{0k}$** (usually the critical volume is one to three times greater than normal volume of liquid). Statistical weight of atoms

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*Here, of course, there also exists an uncertainty connected with the fact that the critical parameters of metallic liquids, as a rule, are unknown.

**Magnitude T_{crit} was estimated in [39]; by the formula of Vander-Waals, critical pressure: $p_{crit} = 3/8 \cdot n_{crit} kT_{crit} \approx 2400$ atm.

of lead is equal to $g_0 = 9$. Calculation with these parameters gives $S_{crit} = 42.8$ cal/mole·deg*.

Entropy in the shock wave may be calculated by using the thermodynamic functions $\varepsilon(T, V)$ and $p(T, V)$ described in § 6. It is simplest of all to find entropy in state T and V by integrating the thermodynamic equation

$$dS = \frac{d\varepsilon + p\,dV}{T} = \frac{d\varepsilon_T + p_T\,dV}{T}$$

at first at constant temperature equal to normal T_0, from normal volume V_0 to V, and then when V = const, with temperature from T_0 to T. In the first integral it is then possible to disregard the electron members, which are insignificantly small at $T_0 \approx 300^\circ$K. Considering, for appraisal, the Grueneisen coefficient to be equal to $\Gamma(V) \approx \Gamma_0 \frac{V}{V_0}^m$, where index m for lead according to Table 11.2 is approximately equal to $m \approx 1$, we obtain as a result of integration

$$S(T, V) = S_0 + c_V \ln \frac{T}{T_0} + \beta_0 \left(\frac{V}{V_0}\right)^{\frac{1}{2}} (T - T_0) - \frac{\varepsilon_0}{mT_0} [\Gamma_0 - \Gamma(V)] \quad {**}). \qquad (11.67)$$

Here S_0 is the entropy of metallic lead under normal conditions T_0, V_0, ε_0, which according to source material [40] is equal to $S_0 = 15.5$ cal/mole × deg. Putting in formula (11.67) the parameters of the shock wave from Table 11.2 we find entropy in the wave. Entropy, close to critical S_{crit}, is attained at the following shock wave

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*Use of the Van-der-Waals equation for calculation of nonideality of a gas leads to very small correction for entropy $\Delta S_{nonid} = R \ln 2/3 = -0.8$ cal/mole·deg (at the same volume at which S ideal is calculated). This correction is introduced into the value of S_{crit}.

**The last member, which depends on Γ, plays a small role, so that the error connected with the approximate interpolation of Γ(V) by exponential formula is not essential.

parameters: $V_0/V_1 = 1.9$, $p_1 = 2.25\cdot10^6$ atm, $T_1 = 15{,}000^\circ K$, $\varepsilon_1 = 4.71\cdot10^{10}$ erg/g*(more exact, with these parameters $S_1 = 44.5$ cal/mole·deg). Energy ε'_t during adiabatic expansion to zero volume V_{0K} turns out to be equal to $1.9\cdot10^{10}$ erg/g, i.e., twice as much as binding energy $U = 0.94\cdot10^{10}$ erg/g, which fully corresponds to the expected magnitude, as this was mentioned above ($T' = 9500^\circ K$, $p'_t = p' \approx 5\cdot10^5$ atm).

Thus, one should expect that in more powerful shock waves during unloading there will occur full evaporation of lead. Let us give for an example certain results of calculation for the most powerful shock waves in lead that were investigated during the experiment. Namely, when $p_1 = 4\cdot10^{12}$ atm, $V_0/V_1 = 2.2$ entropy $S_1 = 51.7$ cal/mole·deg, and energy at the moment of expansion to normal volume $\varepsilon'_t = 3.57\cdot10^{10}$ erg/g, i.e., 3.6 times more than binding energy $U(T' = 15{,}000^\circ K)$. In this case, obviously full evaporation during unloading has already occurred.

In conclusion, let us emphasize that in an unloading wave, spreading through a body after emergence of a shock wave on a free surface, from the very beginning there are particles of the substance in the most diverse states, starting from pressure p_1 (in the head of a rarefaction wave) and to zero (on free surface). In a wave there are represented all states, through which there passes a given particle in the process of evolution from pressure p_1 to zero. Let us also note that the pressure in particles close to the free surface drops so quickly to zero, which in case of full vaporization in this region is strongly supersaturated, although by the conditions of thermodynamic

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*It is curious to note that the energy in a shock wave, at which only full evaporation begins is five times more than the binding energy.

equilibrium the substance had to be in a two-phase state.

§ 23. Experimental Determination of Temperature and Entropy in a Powerful Shock Wave by Means of Investigation of an Unloaded Substance in Gas Phase

Several paragraphs in this chapter were dedicated to the study of the thermodynamic properties of solids at high pressures and temperatures and the description of methods of experimental investigation of these properties by means of measurements of parameters of shock compression of a substance. The general feature of these methods consists which way there can be found only the mechanical parameters of the substance: pressure, density, and full internal energy. Measurement of kinematic parameters of a shock wave — speed of propagation of front and mass speed together with the use of relationships on the front of the shock wave — does not give the possibility to directly determine such important thermodynamic characteristics as temperature and entropy. For finding temperature and entropy according to mechanical measurements it is necessary to have some theoretical diagrams for description of thermodynamic functions. Above we used the trinomial presentation of pressure and energy, where certain parameters, such as heat capacity of atomic lattice, coefficients of electron heat capacity, and electron pressure were determined theoretically.

Meanwhile it would be very interesting and important to find some ways of direct experimental establishment of temperature or entropy in a shock wave, as far as possible reducing the number of theoretical parameters. Unfortunately, in this way it is necessary to meet with large difficulties, both of an experimental and fundamental character. One of the most important methods of measurement of high temperatures, optical, can be used only in the case when the body is transparent, and when the overwhelming majority of solids and in particular, metals, presenting the biggest interest, are non-transparent.

Temperature behind the front of a shock wave was measured by optical means in plexiglas (Ya. B. Zel'dovich, S. B. Kormer, M. V. Sinitsyn, and A. I. Kuryapin [41]). In these experiments they measured the surface brightness of the front of a powerful shock wave that was spreading in a transparent substance, i.e., plexiglas. Then the brightness was re-computed for temperature on the assumption that the heated region, limited by the surface of the front, radiates as an absolute black body. Brightness was measured in the red and blue parts of the spectrum, where there were not only located brightness, but also color temperature (see § 8, Chapter II). In a shock wave with pressure $p \approx 2 \cdot 10^6$ atm and compression $\frac{\rho}{\rho_0} \approx 2.7$ the temperature turned out to be equal to $T \approx 10{,}000$-$11{,}000^\circ$K. Appraisal of temperature according to the internal energy known from mechanical measurements in reasonable assumptions on energy balance (here the dissociation of molecules of plexiglas is essential) testifies to the likelihood of the measured value of temperature.

It would have been possible to try to measure, by optical means, the temperature at the time of emergence of the shock wave on the free surface. However, so that the measured temperature would coincide with the actual temperature in the shock wave, it is necessary to present to the experiment absolutely incredible requirements. In actuality, metals are opaque for visible light in very thin layers $\sim 10^{-5}$ cm. At speed of shock wave of the order 10 km/sec the wave passes a layer of such thickness during the time $\sim 10^{-11}$ sec. Even if it were possible to construct a recording light instrument with colossal resolving power with time $\sim 10^{-12}$ to 10^{-13} sec, in order to catch the moment of emergence of the wave on the surface, when from the surface of the substance the wave is separated by a transparent layer $\sim 10^{-6}$ to 10^{-7} cm, all the same it would be impossible to ensure simultaneity of emergence of the shock wave on the free surface in different points with the required accuracy. In other words, it is impossible to ensure parallelism of surface of front and free surface with a precision of $\sim 10^{-6}$ cm.

If, however, we measure surface glow in a practically acceptable time $\sim 10^{-8}$ sec after the moment of emergence of the shock wave, then glow of the substance will not be registered in the front of the wave, but in an unloading wave, since during the time $\sim 10^{-8}$ sec the unloading wave optically envelopes a very thick layer of the order of 10^{6} cm/sec $\times\ 10^{-8}$ sec $= 10^{-2}$ cm; this layer is absolutely opaque for the light produced in the unloaded region whose temperature is of interest to us. (Question about surface glow of an unloading wave will be considered in detail in the following paragraph).

Fundamental possibilities of experimental determination of temperature (and entropy) in a shock wave were shown in the work of one of the authors in [42]. Let us assume that the shock wave is so strong that after emergence of the wave on the free surface, the substance during unloading is completely evaporated. Then on the front edge of the expanded substance the latter is in gas phase. If by some method we measure in gas phase the mechanical magnitudes: density and pressure, or temperature, then entropy can be calculated theoretically, since the thermodynamic functions of gases are calculated comparatively simply (see Chapter III). But by virtue of the adiabaticness of the process of unloading the entropy of the substance in a shock wave is exactly equal to the entropy in gas phase during unloading. Thus, knowing the entropy in gas phase, we thereby know it also in the shock wave.

In [42] it is shown how it is possible to calculate temperature along the entire adiabat of unloading, if we know the specific internal energy as a function of pressure and density along the adiabat and one value of temperature in any point of the adiabat. Actually, from the thernodynamic identity

$$dS=\frac{de+p\,dV}{T}=\frac{1}{T}\frac{\partial e}{\partial p}dp+\frac{1}{T}\left(\frac{\partial e}{\partial V}+p\right)dV,$$

and the condition that entropy is a function of state, and dS is the total differential, if follows that

$$\frac{\partial}{\partial V}\left(\frac{1}{T}\frac{\partial e}{\partial p}\right)=\frac{\partial}{\partial p}\left[\frac{1}{T}\left(\frac{\partial e}{\partial V}+p\right)\right].$$

Producing differentiation, we obtain, after reductions, a partial differential equation for function T(p, V):

$$\left(\frac{\partial e}{\partial V}+p\right)\frac{\partial T}{\partial p}-\frac{\partial e}{\partial p}\frac{\partial T}{\partial V}=T. \qquad (11.68)$$

The characteristics of this equation áre the lines, the differential equation of which states:

$$\frac{dp}{dV}=-\left(\frac{\partial e}{\partial V}+p\right)\Big/\left(\frac{\partial e}{\partial p}\right).$$

But this is the equation of adiabat. Along the characteristics, i.e., along the adiabat, according to (11.68)

$$\left(\frac{dT}{dV}\right)_s=-T\Big/\left(\frac{\partial e}{\partial p}\right).$$

whence

$$T=T_0\exp\left(-\int\limits_{V_0}^{V}\frac{dV}{(\partial e/\partial p)}\right)=T_0\exp\left(\int\limits_{p_0}^{p}\frac{dp}{\frac{\partial e}{\partial V}+p}\right),$$

where the integrals are selected along the adiabat. This formula also proves the affirmation that was made.

Let us note that knowing the value of entropy in two shock waves similar in amplitude (even not absolute values of entropy, but only their difference), it is easy to calculate the temperature in the shock wave by using the thermodynamic relationship

$$T=\frac{\Delta\varepsilon+p\Delta V}{\Delta S},$$

inasmuch as $\Delta\varepsilon$, p and ΔV are known from mechanical measurements. Exactly so, knowing the values of temperature along the shock adiabat, we can also find the absolute values of entropy by integrating the thermodynamic relationship

$$dS=\frac{d\varepsilon+p\,dV}{T}$$

along the shock adiabat and attaching the constant of integration to the tabular value of entropy of the substance at normal conditions.

§ 24. Vapor Glow of a Metal During Unloading

In the preceding paragraph we noted that an attempt to "see" the high-temperature glow of the front of a powerful shock wave that is spreading through a solid at the time of its emergence on the free surface is doomed to failure. Let us consider in greater detail what should be observed here, what kind of glow will be registered by an instrument directed to the free surface, and how will surface brightness depend on time. Corresponding experiments were set up by S. B. Kormer, M. V. Sinitsyn, and A. I. Kuryapin, and the theory of the phenomenon was given in the work of the authors [43].

Let us assume that a powerful shock wave with temperature in front T_1 on the order of several tens of thousand degrees at the time $t = 0$ emerges on a plane free surface of metal, bordering on a vacuum (surface of the front of the wave is assumed to be strictly parallel to the free surface of the body). The body should be placed in a vacuum; otherwise the unloading substance will push the shock wave ahead of itself in the air, where the temperature of the air will be very high and instead of the metal glow under consideration we will see a glow of high-heated air. The shock wave will be considered so powerful that during unloading the metal is completely evaporated and is expanded in gas phase. Profiles of temperature in initial moment t = 0 and in any subsequent moment of time are depicted in Fig. 11.60. To moment t the wave of rarefaction envelopes a layer of substance with thickness c_1t, where c_1 is the speed of sound in a compressed substance behind the front of a shock wave.

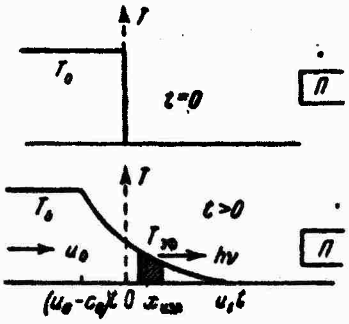

Fig. 11.60. Distributions of temperature at the time of emergence of a shock wave on a free surface t = 0 and in a certain time, when t > 0. Radiating layer is shaded. II — instrument that records light.

Inasmuch as the substance itself moves in a laboratory system of coordinates with speed u_1, the coordinate of the head of a rarefaction wave at the time t is $x = (u_1 - c_1)t$ (to the initial position of free surface we will add the coordinate x = 0). The front edge of the expanding metal vapors flies forward with speed u_2, which is given by formula (11.66). Inasmuch as the substance in an unloading wave is in gas phase, the temperature on the boundary with the vacuum is equal to zero, just as density and pressure.

In the preceding paragraph we said that metals are opaque in very thin layers $\sim 10^{-6}$ cm. This means that already at the moment of time $t \sim 10^{-11}$ sec (at speed $c_1 \sim D \sim 10^6$ cm/sec) the layer of unload metal almost completely shields the high-temperature radiation of temperature T_1, and the metal, preliminarily heated by the shock wave, becomes invisible.

Let us see how the surface of a substance glows in a continuous spectrum and what kind of radiation enters a recording instrument that is directed to a plane free surface. Vapors of the metal constitute a monatomic gas, the optical properties of which in the continuous spectrum were studied in detail in Chapter V. The coefficient of absorption of visible light extraordinarily rarely depends on temperature. It increases rapidly with increase of temperature, whereby the cold vapors are absolutely transparent in the continuous spectrum. Glow of a layer with distribution of temperature similar to that depicted in Fig. 11.60 was already considered in Chapter IX. The phenomenon is absolutely analogous to the glow of air in the heating layer that forms in front of the compression shock in a strong (supercritical) shock wave. At low temperatures on the boundary with a vacuum the vapors are transparent and radiate very weakly. Conversely, in deeper layers, where the temperature is high, the vapors are absolutely non-transparent for visible light and "do not release" the quanta produced in these layers. To "infinity" from the surface of the substance depart the quanta that will be produced in a certain intermediate, radiating layer far from the boundary on the vacuum at an optical distance τ_ν on the order of unity (the radiating layer is shaded in Fig. 11.60).

Knowing the distributions of temprature and density on the coordinate and coefficient $\varkappa_\nu$ of light absorption of a given frequency ν as a function of temperature and density, it is possible to calculate the effective temperature of radiation of this frequency by general formula (2.52).

It is possible, however, to proceed in a simpler manner, noting that effective temperature coincides with temperature of radiating layer (geometric thickness of radiating layer is small and the temperature in it hardly changes), i.e., we can compose an expression for optical thickness, counted off from the boundary on the vacuum, and equate it to unity:

$$\tau_\nu = -\int_{u_2 t}^{x(T_{\text{эф}})} \varkappa_\nu(x)\,dx = 1. \tag{11.69}$$

Passing to the variable of integration, i.e., temperature, we write

$$-\int_{0}^{T_{\text{эф}}} \varkappa_\nu(T)\frac{dx}{dT}\,dT = 1. \tag{11.70}$$

This is also an equation for determination of effective temperature. For calculation of the derivative from the distribution of temperature we shall use the general solution for a rarefaction wave (11.63) and (11.64).

Inasmuch as the substance on the front edge, near the boundary on the vacuum, i.e., exactly in the region where the radiating layer lies, is in gas phase, then, assigning the effective adiabatic exponent of gas γ, we can find the approximate distribution of all magnitudes in this region in clear form. For this we must integrate equation (11.64) not on the side of the compressed substance, as this was done in the derivation of formula (11.65), but on the side of the boundary with the vacuum

$$u = u_2 - \int_0^{p} \frac{dp}{\rho c} = u_2 - \int_0^{\rho} c\,\frac{d\rho}{\rho} \tag{11.71}$$

and use the adiabatic bound $c(\rho, S)$.

The solution will contain, as parameters, the speed of the boundary u_2 and entropy S. We shall not write out this solution, but will find the derivative directly from equation (11.63) and differential relationship $du = -c\, d\rho/\rho$:

$$\frac{1}{t}\frac{dx}{dT} = \frac{\partial u}{\partial T} - \left(\frac{\partial c}{\partial T}\right)_S = -c\left(\frac{\partial \ln \rho}{\partial T}\right)_S - \left(\frac{\partial c}{\partial T}\right)_S,$$

or

$$\frac{dx}{dT} = -\frac{ct}{T}\left\{\left(\frac{\partial \ln \rho}{\partial \ln T}\right)_S - \left(\frac{\partial \ln c}{\partial \ln T}\right)_S\right\} \sim -\frac{\gamma+1}{2(\gamma-1)}\frac{ct}{T}.$$

Here we used the relationship $c \sim \sqrt{T}$, and also the adiabatic bond $T \sim \rho^{\gamma-1}$.

Equation (11.70) now takes on the form:

$$\frac{\gamma+1}{2(\gamma-1)}\, t \int_0^{T_{ef}} \varkappa_\nu(T)\frac{c(T)}{T}\, dT = 1. \qquad (11.72)$$

Hence it is clear that with the passage of time, the integral an consequently, also the effective temperature of radiation decrease.

The physical cause of this consists in that with the passage of time, when the unloading wave envelopes an even greater and larger mass of substance, the geometric and optical thicknesses of the layer between the boundary on the vacuum and the point with given temperature continuously increase. Therefore, the radiating layer, distance from the boundary at an assigned optical distance on the order of unity, moves into a region of even lower temperatures (Fig. 11.61)

It is remarkable that from equation (11.72) for the dependence $T_{ef}(t)$ the speed of the boundary u_2 fell*, which to us is unknown, since it is determined by the thermodynamic functions of the substance along the entire adiabat of unloading, including the unexplored region where density is somewhat less than the normal density of a solid. As

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*Since in expression (11.70) coordinate x does not enter in clear form, but only derivative $\frac{dx}{dt}$.

a parameter in equation (11.72) there enters only entropy S, owing to the dependence of the coefficient of absorption $\varkappa_\nu$ on density (number of atoms per cm^3 - n), which is connected with temperature by the adiabatic equation:

$$n = B(S) T^{\frac{1}{\gamma-1}}, \tag{11.73}$$

where B(S) is the entropy constant.

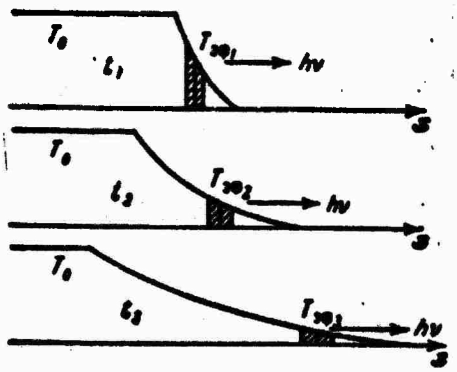

Fig. 11.61. Shift of radiating layer (shaded) in an unloading wave with the passage of time.

If the basic mechanism of absorption of visible light in vapors of metals is photoelectric absorption by highly excited atoms (and also deceleration absorption in the field of ions), the coefficient of absorption $\varkappa_\nu$ can be approximately calculated by formula (5.44):

$$\varkappa_\nu = \frac{a_\nu n}{T^2} e^{-\frac{I-h\nu}{kT}}, \tag{11.74}$$

where a_ν is a constant depending on frequency; ($a_\nu \sim \nu^{-3}$); I is the ionization potential.

There are indications of the fact that in dense vapors of heavy atoms an essential role is played by deceleration absorption in the field of neutral atoms. In the work of L. M. Biberman and V. Ye. Romanov [44] it is shown that in mercury tubes of high pressure, evidently, this mechanism of light absorption is the main one (see § 7, Chapter V). In this case the coefficient of absorption $\varkappa_\nu$ is proportional to the number of free electrons n_e, i.e., the degree of ionization, and the basic temperature dependence of the coefficient of absorption also has a Boltzmann character, but with another exponential index

$$\varkappa_\nu \sim n n_e = b_\nu e^{-\frac{I}{2kT}} n^{\frac{3}{2}}, \tag{11.75}$$

where b_ν weakly depends on temperature (as $T^{3/4}$).

At present it is difficult to say which of the mechanisms of absorption plays a larger role. In any case, the general character of the temperature dependence of $\varkappa_\nu$ in both cases is identical $\varkappa_\nu \sim e^{-E/kT}$ where $E = I - h\nu$ in the first case and $E = I/2$ in the second. It should be mentioned that numerically both values of E do not differ much for metals (when $I \approx 6$-8 ev, $h\nu \approx 2$-3 ev).

Let us approximately calculate the integral in formula (11.72) taking into account that the basic dependence of the integrand expression on temperature is included in the exponential factor. Considering all slowly changing exponential temperature factors to be constant, we shall obtain $te^{-E/kT_{ef}} = \text{const}$, i.e., we obtain the logarithmic drop of effective temperature of radiation in time (Fig. 11.62):

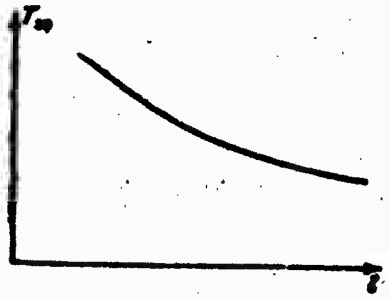

Fig. 11.62. Dependence of effective (brightness) temperature of the surface of an unloading wave on time.

$$T_{\text{эф}} = \frac{\text{const}}{\ln t + \text{const}'}.$$

Specific calculations show that for metals, independently of the assumption on any of enumerated mechanisms of absorption, the effective temperature is of the order of 7000-4000°K in moments $t \sim 10^{-7} - 10^{-6}$ sec* (in this time the free surface departs noticeably to 10^{-1} - 1cm at speeds ~10 km./sec).

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*Whereas in a shock wave the temperature T_1 can be tens of thousand degrees.

§ 25. Remarks on the Fundamental Possibility of Measurement of Entropy in a Shock Wave According to Glow During Unloading

Equation (11.72) contains only one parameter that characterizes the shock wave, i.e., entropy S. If we know the optical properties of the substance, i.e., function $\varkappa_\nu(T, \rho)$, then, experimentally taking the curve of glow $T_{ef}(t)$, we can find the absolute value of entropy in the shock wave. Conversely, assigning values of entropy from other considerations (calculating it with the help of thermodynamic functions of compressed solid matter and measured parameters of the shock wave), it is possible, from the experiment on glow of an unloading surface, to extract data on the optical properties of vapors of metals, and namely, to determine the preexponential factor in the expression for coefficient of absorption. It is curious to not that on the assumption that there exists only one mechanism of absorption and $\varkappa_\nu$ is expressed either by formula (11.74) or (11.75), in the final equation for function $T_{ef}(t)$, which is obtained upon integration of (11.72), there enters only the product of unknown parameters $a_\nu B(S)$ in the case of (11.74) and $b_\nu B^{3/2}(S)$ in the case of (11.75) (since in (11.74) $\varkappa_\nu \sim a_\nu n \sim a_\nu B$, and in (11.75) $\varkappa_\nu \sim b_\nu n^{3/2} \sim b_\nu B^{3/2}$). Entropy constant B in adiabatic equation (11.73) depends on the absolute value of entropy S as $B \sim e^{-S/R}$ (R is the gas constant).

This means that by taking curves of glow in two experiments with somewhat differing amplitudes of shock waves and determining the parameters, let us say, the product $a_\nu B$, we thereby find the difference of entropies in shock waves, even not knowing the optical constant a_ν:

$$\frac{a_\nu B'}{a_\nu B''} = \exp\left[-\frac{S' - S''}{R}\right].$$

where one prime and two primes pertain to the first and second experiments. By the difference of entropies, as was noted in the preceding paragraph, we can also find the temperature in a shock wave.

The described experiment can serve as the specific embodiment of the considerations expressed in the preceding paragraph about the use of measurements in gas phase in an unloading wave for the experimental determination of entropy and temperature in a shock wave.

5. Some Other Phenomena

§ 26. Electrical Conductivity of Nonmetallic Bodies in Shock Waves

Under usual conditions gases are good insulators. In sufficiently strong shock waves they become conductors. Something similar also occurs with solid dielectrics, which in strong shock waves conduct electrical current.

However, if in gases the approach of conductivity is connected simply with thermal ionization, which takes place at high temperatures of the order of ten thousand degrees and above, obtainable in a shock wave, the physical cause of transformation of solid dielectrics into conductors in shock waves is considerably more complicated, is connected more quickly with compression than with increase of temperature, and in many respects is still not clear.

Electrical conductivity of condensed substances in a shock wave was studied by several authors. A. A. Brish, M. S. Tarasov, and V. A. Tsukerman developed a method and measured the conductivity of products of detonation of condensed explosives [45], and also water, organic glass, and paraffin [46],* in strong shock waves with pressures up

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*The conductivity of air was also studied in this work.

to a million atmospheres. Conductivity of an ionic crystal of sodium chloride at pressures up to a million atmospheres was studied in the above-cited work [5]. Weaker shock waves (to 250,000 atm) were worked with by Alder and Christian who measured electrical conductivity of ionic and molecular crystals of CsJ, J_2, CsBr, $LiAlH_4$, and others [47].

The essence of the basic electric-contact method, described in article [45], with the help of which were measured conductances in [45, 46, and 5], consists of the following. In a body, through which there spreads a shock wave, there are introduced electrodes (contacts) K, united by shunting resistor R_{sh} (Fig. 11.63). Until the shock wave not approaches the contacts, the resistance of the substance, i.e., the dielectric, is practically infinite. After the shock wave reaches the contacts the dielectric becomes a conductor, and the unknown resistor R_x is parallel connected to resistor R_{sh}.

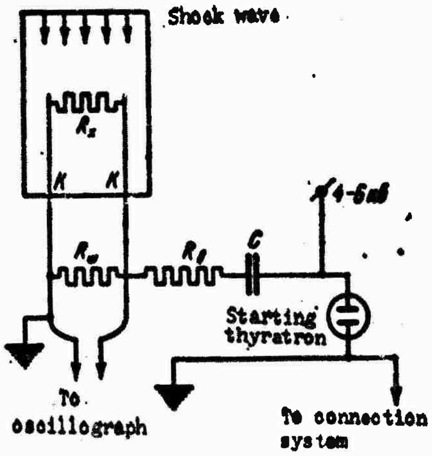

Fig. 11.63. Diagram of an experiment on the measurement of electrical conductivity in a shock wave.

Shortly before the approach of the shock wave to the contacts, through the high-voltage resistor R_{hv} and contacts, capacitor C discharges. The capacitor is preliminarily charged to a high voltage of several kilovolts (this is done with the help of the starting thyratron). Resistor $R_{hv} \gg R_{sh}$, so that the current in the network is determined only by resistor R_{hv}. The potential difference on contacts is proportional to the resistance between contacts. The latter is equal to R_{sh} until approach of the shock wave and $R = R_{sh}R_x/(R_{sh} + R_x)$ after the shock wave reaches the contacts (resistor R_{sh} is selected in such a manner so that it is of the order of R_x).

If U_{sh} and U_x correspond to the potential difference on the contacts, then $U_{sh}/U_x = R_{sh}/R = (R_{sh} + R_x)/R_x$. Voltages U_{sh} and U_x are measured by an oscillograph; R_{sh} is known; unknown resistance R_x is calcualted with the help of this formula.

For transition from measured resistance R_x to conductivity of the substance electrolytic simulation is applied. For this the electrodes, under the exact observance of geometry of the experience, are dipped into an electrolytic bath. By changing the density of the electrolyte we obtain a resistance equal to that measured in the experiment. The unknown conductivity is equal to the known conductivity of the electrolyte (for other methods of measurement of conductivity of substance in a shock wave see [45,5]).

Experiments [46] showed that electrical conductivity of dielectrics in a shock wave is increased by many orders. If initial conductivity of distilled water composed $\sigma \sim 10^{-5}$ ohm^{-1} cm^{-1}, then at pressure $p = 10^5$ atm there would be obtained $\sigma = 0.2$ ohm^{-1} cm^{-1}. Conductivity in the shock wave absolutely did not depend on initial conductivity of the water, connected with impurities. The same value of σ in a shock wave was also obtained for ordinary water with conductivity $\sigma \sim 10^{-3}$ ohm^{-1} cm^{-1}.

Such perfect dielectrics as paraffin ($\sigma \sim 10^{-18}$ ohm^{-1} cm^{-1}) and organic glass ($\sigma \sim 10^{-15}$ ohm^{-1} cm^{-1}) at pressures of the order of 10^6 atm were transformed into fair conductors with conductivity $\sigma \sim 1$ to $2 \cdot 10^2$ ohm^{-1} cm^{-1}.*

In paraffin a noticeable increase of conductivity is observed at pressures ~ 6-$7 \cdot 10^5$ atm and upon further increase of pressure σ

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*For comparison with metallic conductivity let us indicate that in copper $\sigma \sim 10^6$ ohm^{-1} cm^{-1}, in iron $\sigma \sim 10^5$ ohm^{-1} cm^{-1}, and in mercury $\sigma \sim 10^4$ ohm^{-1} cm^{-1}.

grows rapidly. In organic glass there occurs an extraordinarily sharp growth of conductivity at pressure $8 \cdot 10^5$ atm.

Change of electrical conductivity of organic glass and paraffin in a shock wave by 15-20 orders confirms the "metallization" of these dielectrics during compression to pressures of the order of a million atmospheres.*

The phenomenon is impossible to explain by thermal ionization. It is connected with change of structure of the electron zones of a solid during compression. During compression, the zones draw near, and the distances between them decrease, thereby facilitating the electron transitions leading to the appearance of free electrons and metallic conductivity in the substance earlier than in the former dielectric.**

Qualitative considerations concerning the metallization of any substance during sufficiently strong compression were discussed by Ya. B. Zel'dovich and L. D. Landau [48], where they considered the transition of metals from solid in gaseous state (metallization of hydrogen at large densities was studied A. A. Abrikosov [49]).

It should be said that the components of the mechanism of metallization of dielectrics in a shock wave are still not fully clear, and this phenomenon requires further theoretical and experimental study. In particular, it is interesting to separately establish the roles of

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*In the experiments of Alder and Christian [47] they measured considerably smaller electrical conductivities. The phenomenon of "metallization" in those comparatively weak waves which these authors worked with, was expressed much weaker.

**Influence of pressure on electrical conductivity of dielectrics was studied earlier (in the region of comparatively small pressures). Thus, Bridgeman [50] established that yellow phosphorus, which is a dielectric, at pressures $1.2\text{-}1.3 \cdot 10^4$ atm and temperature 200°C changes into a new modification, i.e., black phosphorus, which has metallic conductivity. The density of black phosphorus is 1.4 times more than that of yellow.

temperature and compression in the increase of conductivity.

Experiments [5] with sodium chloride, which under normal conditions possesses small ionic conductivity, permit the consideration that a basic role in the increase of electrical conductivity with increase of amplitude of shock wave, in distinction from the preceding, is played by temperature. Curve of the dependence $\sigma(T)$ has a Boltzmann character $\sigma \sim e^{-E/kT}$ with activation energy $E \approx 1.2$ ev, which obviously also confirms the ionic nature of conductivity of NaCl in a shock wave.

Numerically, on the boundaries of the investigated interval of amplitudes when $p = 10^5$ atm, $T = 440^\circ K$, $\frac{V_0}{V} = 1.26$, $\sigma = 2 \cdot 10^{-5}$ ohm^{-1} cm^{-1}; when $p = 7.9 \cdot 10^5$ atm, $T = 6150^\circ K$, $\frac{V_0}{V} = 1.85$, and $\sigma = 3.26$ ohm^{-1} cm^{-1}.

§ 27 Measurement of the Refraction Index of a Substance Compressed in a Shock Wave

The width of the front of a shock wave in solids and liquids is comparable with the interatomic distances and much less than the wavelengths of visible light $\lambda \sim 4000\text{-}7300$ Å. Therefore, a light, passing through a transparent undisturbed substance and falling on the surface of the front of a shock wave, which separates the undisturbed substance from the compressed, is reflected also, as from the usual boundary of two different media. Reflection of light from the surface of the front of a shock wave in transparent bodies, water, and plexiglas was investigated in experiments set up by Ya. B. Zel'dovich, S. B. Kormer, M. V. Sinitsyn, and K. B. Yushko [51].

Knowing the refraction index of an undisturbed substance and the angle of incidence, and measuring the reflectivity, it is then possible by known Fresnel formulas (see, for instance [52]) to calculate the refraction index n of a substance compressed by a shock wave.*

This method in general is also applicable when the substance compressed by the shock wave is not transparent. If the range for absorption is comparable with the wavelength of light, when in principle it is possible to also measure the real and imaginary parts of the refraction index. For this it is necessary to determine the dependence of reflectivity on the angle of incidence and polarization of reflected light [54].

In a sufficiently strong shock wave that is transparent in undisturbed state the substance becomes non-transparent. Disturbing of transparency at high pressures can occur for various reasons: due to cracking of the substance, because of phase transitions, and owing to rearrangement of electron levels, in particular during "metallization" of dielectrics, which was mentioned in the preceding paragraph.

A fundamental diagram of experiments [51] on the study of reflection of light from the front of a shock wave in water is shown in Fig. 11.64.

The plane surface of the end of the explosive charge touches a plexiglas plate on which there has been applied a layer of water. Over the water there is placed a plexiglas prism. Movement of the beams before the explosion is shown in Fig. 11.64a. On the prism there

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*In gases the width of the front of a shock wave, i.e., the thickness of the transition layer between undisturbed and compressed substances, is of the order of the wavelength of light; therefore the Fresnel formulas are inapplicable here: However, in gases the refraction index at various densities is known. Study of reflection of light in these conditions permits the determination of width of the front of a shock wave. Such measurements were made by Hornig and Cowan [53] for shock waves of weak intensity (see Chapter IV).

drops beam I from the source of light and from it there emerge beams reflected from two surfaces of water II and III.

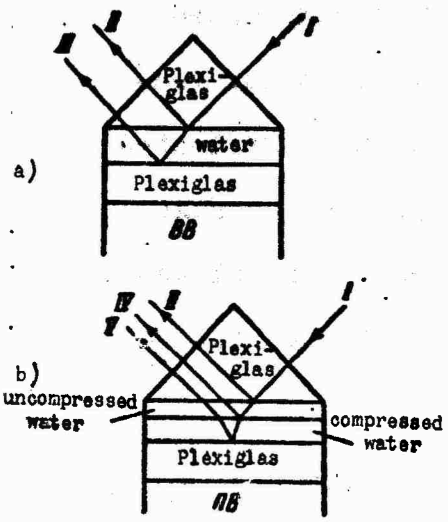

Fig. 11.64. Diagram of an experiment on the measurement of reflection of light from the front of a shock wave: a) before explosion; b) in the process of propagation of the shock wave through water.

Movement of beams after explosion and emergence of the shock wave into the water is shown in Fig. 11.64b. Reflection from the surface of the front of the shock wave is given by beam IV and reflection from the moving boundary between the plexiglas sublayer and compressed water by beam V. Beam V now replaces beam III. Reflected beams are recorded by photographic means with time scanning. A diagram of the photograph is shown in Fig. 11.65. Before blasting, beams II and III give straight light lines on moving film. At the time t_1 of emergence of the shock wave into the water there appear two lines, from beams IV and V, where line V now replaces completed line III. Line II continues, remaining constant up to emergence of the shock wave on the upper surface of water (moment t_2). As can be seen from Fig. 11.64b, according to approach of the front of the wave to the upper boundary of water, the distance between beams IV and II decreases. At the time of emergence t_2 beams IV and II coincide; line IV in Fig. 11.65 reaches line II.

The distance between beams II and III in nature were approximately 20 mm, and the difference of times $t_2 - t_1 \sim 4 \cdot 10^{-6}$ sec.

Speed of the front of the shock wave in water was measured by the slope of line IV. Knowing the shock adiabat of water, one can determine density and other parameters behind the front. Reflectivity was computed by the ratio of intensities of incident and reflected beams; intensities were determined by photometric means.

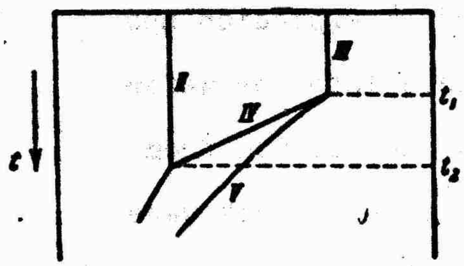

Fig. 11.65. Diagram of photochronogram.

The refraction index of compressed water was determined by two methods: geometric (by the distances between reflected beams) and by reflectivity. The average values in several experiments, calculated by this and another method, turned out to be close to one another.

Within the limits of change of density of water from $\rho/\rho_0 = 1.47$ to $\rho/\rho_0 = 1.81$, which corresponds to pressures from 50 to 150 thousand atm, the refraction index almost does not change and is equal to $n = 1.49 \pm 0.03$ (by geometric method) and $n = 1.46 \pm 0.03$ (by reflection). In water of normal density $n = n_0 = 1.333$. Experimental results of other authors on the measurement of the refraction index of water at small pressures are quite well described by the linear dependence $n = 1 + 0.334\,\rho$,* where ρ is the density in g/cm^3. This formula will agree with the data for steam and also the index of refraction of ice at 0°C and $\rho = 0.92$, equal to 1.311.

The value of the indices which are obtained for water compressed in a shock wave are noticeably lower than the values dictated by the given formula.

In all probability, the divergence should be blamed on the effect of temperature (during compression by shock wave to density $\rho = 1.8\,\rho_0$ water was heated to 1100°C). The mechanism of the influence

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*The Lorenze — Lorentz formula gives much worst agreement with the experiment.

of temperature (the higher the temperature, the lower the refraction index) still remains unclarified.

Investigations of reflection of light from the front of a shock wave showed that the surface of the front is smooth (otherwise reflection would be diffuse, and not mirror).

Literature

1. L. V. Al'tshuler, K. K. Krupnikov, B. N. Ledenev, V. I. Zhuchikhin, and M. I. Brazhnik. ZhETF, 34, 874 (1958).

2. L. V. Al'tshuler, K. K. Krupnikov, and M. I. Brazhnik. ZhETF, 34, 886 (1958).

3. L. V. Al'tshuler, S. B. Kormer, A. A. Bakanova, and R. F. Trunin. ZhETF, 38, 790 (1960).

4. L. V. Al'tshuler, S. B. Kormer, M. I. Brazhnik, L. A. Vladimirov, M. P. Speranskaya, and A. I. I. Funtikov. ZhETF, 38, 1061 (1960).

5. L. V. Al'tshuler, L. V. Kuleshova, and M. N. Pavlovskiy. ZhETF, 39, 16 (1960).

6. G. L. Shnirman, A. S. Dubovik, and P. V. Kevlishvili. High-speed photorecording installation SFR, Publishing House of the Institute of Technical-Economic Information, AN SSSR (1957).

7. A. S. Dubovik. Journal of Scientific and Applied Photography and Cinematography, 2, 293 (1957); 4, 226 (1959).

8. A. S. Dubovik, P. V. Kevlishvili, and G. L. Shnirman. Time magnifier of 33 million frames per second. Report at the 4th International Congress on High-speed Photography and Cinematography, Cologne, 1958.

9. G. L. Shnirman. Progress of scientific photography, 6, 93 (1959).

10. A. S. Dubovik. Progress of scientific photography, 6, 102 (1959).

11. V. A. Tsukerman and M. A. Manakova. Pulse X-ray tubes operating on 1 to 2 million volts. Reports at the 4th International Congress on High-speed Photography and Cinematography, Cologne, 1958.

12. M. M. Butelov and Ye. K. Zavoyskiy, et al. EOP's of the type PIM-3 and PIM-4. Reports at the 4th International Congress on High-speed Photography and Cinematography, Cologne (1958).

13. P. Combash. Statistical theory of the atom and its application, IL, 1951.

14. S. B. Kormer and V. D. Urlin. DAN SSSR, 131, 542 (1960).

15. S. B. Kormer, V. D. Urlin, and L. T. Popov. FTT, 3, 2131 (1961).

16. L. Landau and Ye. Lifshits. Statistical physics, State Technical Press, 1951.

17. J. C. Slatter. Introduction in the Chemical Physics, McGraw Book Company, Inc., New york, London, 1939.

18. L. D. Landau and K. P. Stanyukovich. DAN SSSR, 46, 399 (1945).

19. J. J. Gilvarry. Phys. Rev., 96, 934, 944 (1954). J. J. Gilvarry and G. H. Reebles. Phys. Rev., 99, 500 (1955).

20. R. Latter. Phys. Rev., 99, 1854 (1955).

21. F. A. Baum, K. P. Stanyukovich, and B. I. Shekhter. Theory of explosives, Part I, 1952; Physics of explosion, Fizmatgiz, 1959.

22. J. M. Walsh and R. H. Christian. Phys. Rev., 97, 1544 (1955).

23. J. M. Walsh, M. H. Rise, R. G. McQueen, and F. L. Yarger. Phys. Rev., 108, 196 (1957).

24. W. Goranson and D. Bankroft et. al., J. Appl. Phys., 26, 1479 (1955).

25. D. Mallory. J. Appl. Phys., 26, 555 (1955).

26. R. G. McQueen and S. P. Marsh. J. Appl. Phys., 31, 1253 (1960).

27. J. S. Dugdale and D. K. McDonald. Phys. Rev., 89, 832 (1953).

28. L. D. Landau and Ye. M. Lifshits. Mechanics of solid matter, 2nd Publication, State Technical Press, 1954.

29. Kh. A. Rakhmatullin and G. S. Shapiro. News of the Academy of Sciences of the USSR, OTN, No. 2, 68 (1955).

30. B. Bancroft, E. Peterson, and S. Minshall. J. Appl. Phys., 27, 291 (1956).

31. R. E. Duff and S. Minshall. Phys. Rev., 108, 1207 (1957).

32. W. E. Drummond. J. Appl. Phys., 28, 998 (1957).

33. A. N. Dremin and G. A. Adadurov. DAN SSSR, 128, 261 (1959).

34. A. N. Dremin. PMTF, No. 3, 184 (1960).

35. B. J. Alder and R. H. Christian. Phys. Rev. Letters, 4, 450 (1960)

36. I. M. Lifshits. ZhETF, 38, 1569 (1960).

37. G. M. Gandel'man. ZhETF, 43, 131 (1962).

38. A. I. Ivanov and S. A. Novikov. ZhETF, 40, 1880 (1961).

39. S. N. Zasumkin. Engineering-Physics Journal, 3, 63 (1960).

40. Chemist's Handbook, Vol. I, State Chemistry Press, 1951.

41. Ya. B. Zel'dovich, S. B. Kormer, M. V. Sinitsyn, and A. I. Kuryapin. DAN SSSR, 122, 48 (1958).

42. Ya. B. Zel'dovich. ZhETF, 32, 1577 (1957).

43. Ya. B. Zel'dovich and Yu. P. Rayzer. ZhETF, 35, 1402 (1958).

44. L. M. Biberman and V. Ye. Romanov. Optics and spectroscopy, 3, 646 (1957).

45. A. A. Brish, M. S. Tarasov, and V. A. Tsukerman. ZhETF, 37, 1543 (1959).

46. A. A. Brish, M. S. Tarasov, and V. A. Tsukerman. ZhETF, 38, 22 (1960).

47. B. J. Alder and R. H. Christian. Phys. Rev., 104, 550 (1956).

48. Ya. B. Zel'dovich and L. D. Landau. ZhETF, 14, 32 (1944).

49. A. A. Abrikosov. Astronomical Journal, 31, 112 (1954).

50. P. V. Bridzhmen. Physics of high pressures, ONTI, 1935; Latest works in the area of high pressures, IL, 1948.

51. Ya. B. Zel'dovich, S. B. Kormer, M. V. Sinitsyn, and K. B. Yushko. DAN SSSR, 138, 1333 (1961).

52. L. D. Landau and Ye. M. Lifshits. Electrodynamics of solid matter, State Technical Press, 1957.

53. J. R. Cowan and D. F. Hornig. J. Chem. Phys., 18, 1008 (1950).

54. V. P. Ginzburg and G. P. Motulevich. UFN, 55, 469 (1955).

CHAPTER XII

CERTAIN SELF-SIMILAR PROCESSES IN GAS DYNAMICS

1. Introduction

§ 1. Transformation Groups Allowed by Equations of Gas Dynamics

In Chapter I we already became familiar with several examples of self-similar motions (with the self-similar wave of rarefaction, with the problem about the powerful explosion.* In this chapter we will study in detail the self-similar motion of one of two basic types. In the introductory section of the chapter, we will show how in equations of gas dynamics the possibility of existence of self-similar solutions is expressed and we will give the common characteristics, of self-similar motions. It is expedient preliminarily to become familiar with the common group properties of equations of gas dynamics.

We will consider one-dimensional adiabatic motions of an ideal gas with constant heat capacity, i.e., motions possessing plane, cylindrical, or spherical symmetries. Let us write out a system of equations for these types of motions. In continuity equation (1.2) we open the sign of divergence and present the equation in a single

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*In Chapter X we considered self-similar problems of the theory of propagation of heat by the mechanism of thermal conduction in a motionless substance.

form, common for all three forms of symmetry; furthermore, we will divide the entire equation by density ρ. In adiabatic equation (1.13) we place the expression for entropy (1.14) (replacing specific volume by density). Equation of motion (1.6) will remain without changes. Let us obtain the following system of equations for density, pressure, and speed as coordinate and time functions:

$$\left.\begin{aligned}\frac{\partial\ln\varrho}{\partial t}+u\frac{\partial\ln\varrho}{\partial r}+\frac{\partial u}{\partial r}+(\nu-1)\frac{u}{r}=0,\\ \frac{\partial u}{\partial t}+u\frac{\partial u}{\partial r}+\frac{1}{\varrho}\frac{\partial p}{\partial r}=0,\\ \frac{\partial}{\partial t}\ln p\varrho^{-\gamma}+u\frac{\partial}{\partial r}\ln p\varrho^{-\gamma}=0.\end{aligned}\right\}\qquad(12.1)$$

Number ν in the continuity equation is equal to $\nu = 1, 2, 3$ for plane, cylindrical, and spherical cases correspondingly. Variable r plays the role of coordinate x in the plane case and radius in the cylindrical and spherical cases.

Equations (12.1) allow several transformation groups which we will now enumerate. It is assumed that simultaneously with the transformations in the equations analogous transformations are made both in the initial and boundary conditions of the problem.

1) Time t enters the equations only under the sign of the differential, and consequently, the time shift, accomplished by means of introduction of the new variable $t' = t + t_0$, does not change the equations. The possibility of a time shift is connected with the arbitrariness in selection of the beginning of the time reading.

2) In the plane case ($\nu = 1$) the coordinate also enters the equations only under the sign of the differential. Therefore in the plane case there is also possible a coordinate shift connected with the arbitrariness in selection of the beginning of the coordinate reading. Introduction of variable $x' = x + x_0$ does not change the equations.

In the spherical and cylindrical cases this is impossible, since the radius enters the continuity equation not only under the sign of the differential.

Equations of gas dynamics contain five dimensional magnitudes: ρ, p, u, r, t, from which three possess independent dimension. For instance, if one were to select as the basic dimensional magnitudes density, coordinate, and time, the dimensions of speed and pressure are in the form of $[u] = [r]/[t]$; $[p] = [\rho][r^2]/[t^2]$. In accordance with the existence of three independent dimensional magnitudes the equations permit three independent transformation groups of similarity, which are connected with the arbitrariness in selection of units of measurement of the basic dimensional magnitudes.

1) Let us assume that functions $\rho = f_1(r, t)$, $p = f_2(r, t)$, and $u = f_3(r, t)$ constitute the solution of equations for a certain defined motion. Let us change the scale of density, not changing the scales of coordinate and time, for which we introduce new variables $\rho' = k\rho$, $p' = kp$, leaving the rest without change. The equations will not be changed. If we simultaneously change in the same form the intial and boundary conditions, increasing density and pressure k times, the new motion will be described by the functions

$$\rho' = kf_1(r, t), \; p' = kf_2(r, t), \; u = f_3(r, t).$$

The new motion is like the old, differing only by scales of density and pressure.

2) Let us change the scale of length, not changing the scales of density and time. The equations do not change, if we cross in them to new variables: $r' = mr$, $u' = mu$, $p' = m^2p$, leaving the others, ρ and t, without change: $\rho' = \rho$, $t' = t$. This means that if some motion is described by functions $\rho = f_1(r, t)$, $p = f_2(r, t)$,

$u = f_3(r, t)$, by means of simple change of scales it is also possible to describe the new motion, in which the distances and speeds are increased m times, and pressure is increased m^2 times (density remains constant). The solution for the new motion are the functions:

$$\rho' = f_1(r', t), \quad p' = m^2 f_2(r', t), \quad u' = m f_3(r', t).$$

3) Finally, we will change the scale of time, not changing the scales of length and density. The equations allow this transformation:

$$t' = nt, \quad u' = \frac{u}{n}, \quad p' = \frac{p}{n^2}, \quad \rho' = \rho, \quad r' = r.$$

This means that if in initial and boundary conditions the speeds are decreased n times and pressure n^2 times, leaving density constant, the new process will be like the old one, but will only be n times slower.

By means of consecutive application of three transformation groups of similarity one can obtain solutions for an infinite number of new motions with modified scales of density, length, and time. In particular, if we simultaneously extend length and time an identical number of times $r' = lr$, $t' = lt$, the solution will remain constant.

Such transformation is equivalent to consecutive application of transformations 2) and 3) with $m = n = l$. In symbolic form this is possible to record so:

$$u(r, t) \longrightarrow lu(lr, t) \longrightarrow \frac{1}{l} \cdot lu(lr, lt) = u(lr, lt)$$

and analogously for other functions, ρ and p.

§ 2. Self-Similar Motions

In the preceding paragraph it was shown that equations of gas dynamics allow similarity transformations, i.e., there are possible different motions which are similar to each other and can be obtained from one another by means of change of the main scales of length, time, and density. Regarding, however, the given motion, it can be described by the most diverse functions of two variables r and t: $\rho(r, t)$, $p(r, t)$, $u(r, t)$, including also the parameters which enter the initial and boundary conditions of the problem (and adiabatic exponent γ).

There exist, however, such motions, the distinctive property of which is the similarity conserved in the actual motion. Such motions are called self-similar. Distribution of any of gas-dynamic magnitudes with respect to coordinate, let us say, pressure p, in self-similar motion evolves in time in such a way that are changed only the scale of pressure $P(t)$ and coordinate scale of the region enveloped by the motion $R(t)$, but the shape of the profile of pressure remains constant. By means of extension and reduction of scales P and R it is possible to reach exact coincidence of curves $p(r)$, responding to different moments of time t. Function $p(r, t)$ can be presented in the form of $p(r, t) = P(t)\pi(r/R)$, where the dimensional scales P and R somehow depend on time, and dimensionless ration $p/P = \pi(r/R)$ is a "universal" (in the sense of independence on time) function of the new dimensionless coordinate $\xi = r/R$.

By extending and reducing scales P and R in accordance with their dependence on time, it is possible from the "universal" function $\pi(\xi)$ to obtain a true curve of pressure distribution with respect to coordinate $p(r)$ for any moment of time t. Likewise expressed are the other gas-dynamic magnitudes: density and speed.

For self-similar motions the system of equations of gas dynamics in partial derivatives reduces to a system of ordinary differential equations with respect to new unknown functions of self-similar variables $\xi = r/R$.

We shall work out these equations. For this we shall present the solution of partial differential equations (12.1) in the form of the products of scale functions by new unknown functions of the new self-similar variable ξ:

$$\xi=\frac{r}{R},\quad R=R(t). \tag{12.2}$$

Scales of pressure, density, speed, and length are not all independent upon one another. If one were to select as the main scales of length R and density ρ_0, as the scale of speed it is possible to take the magnitude $\frac{dR}{dt} \equiv R$, and as the scale of pressure $\rho_0 R^2$. This does not disturb community and the scale is determined with an accuracy of the numerical coefficient, which is always possible to include in the new unknown function. We shall find the solution in the form

$$p=\rho_0\dot{R}^2\pi(\xi),\quad \rho=\rho_0 g(\xi),\quad u=\dot{R}v(\xi), \tag{12.3}$$

where π, g, and v are new, dimensionless functions of self-similar variable ξ, for which one should compose differential equations. These functions are sometimes called representatives of pressure, density, and speed, correspondingly. Scales of R, ρ_0, and R somehow depend on time, although in an unknown manner.

We shall place expression (12.3) in equation (12.1), take into account the determination of self-similar variable (12.2), and shall use the rules of differentiation of the type:

$$\left.\begin{aligned}&\frac{\partial\rho}{\partial t}=\frac{d\rho_0}{dt}\cdot g-\rho_0\frac{dg}{d\xi}\frac{r}{R^2}\frac{dR}{dt}=\dot{\rho}_0 g-\rho_0 g'\xi\frac{\dot{R}}{R},\\&\frac{\partial\rho}{\partial r}=\frac{\rho_0 g'}{R}\end{aligned}\right\}$$

(differentiation of scales in time is designated by the dot, and differentiation of representatives with respect to self-similar variable, by the prime).

As a result, after simple transformations we obtain the equations:

$$\left.\begin{aligned} \frac{\dot\rho_0}{\rho_0}+\frac{\dot R}{R}\left[v'+(v-\xi)(\ln g)'+(\nu-1)\frac{v}{\xi}\right]=0,\\ \frac{R\ddot R}{\dot R^2}v+(v-\xi)v'+\frac{\pi'}{g}=0,\\ \frac{R}{\dot R}\frac{d}{dt}(\ln\rho_0^{1-\gamma}\dot R^2)+(v-\xi)(\ln\pi g^{-\gamma})'=0.\end{aligned}\right\} \tag{12.4}$$

So that presentation (12.3) is meaningful and it is possible to write differential equations for new unknown functions $\pi(\xi)$, $g(\xi)$, and $v(\xi)$, it is necessary to divide variables t and ξ in equations (12.4). For this, in the second equation one should put $R\ddot{R}/\dot{R}^2$ = const, whence (when const $\neq$ 1)

$$R=At^{\alpha}. \tag{12.5}$$

Here A and α are certain constants (A — dimensional, α — number).

In the first equation of (12.4) it is necessary to put $\frac{\dot\rho_0}{\rho_0}$ = = const $\frac{\dot R}{R}$, which gives

$$\rho_0=Bt^{\beta}, \tag{12.6}$$

where B and β are also constants. The first member in the third equation of (12.4) then is turned into a constant automatically.

Thus, all scales in self-similar motion depend on time according to root laws, and the self-similar variable has the form*

$$\xi=\frac{r}{R}=\frac{r}{At^{\alpha}} \tag{12.7}$$

Equations (12.4) are now transformed into a system of three ordinary differential equations with respect to three unknown functions $\pi(\xi)$, $g(\xi)$, and $v(\xi)$. The system contains exponents: constant numbers α and β. In an analogous way the initial and boundary conditions of the problem, will be converted to dimensionless form. They

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*As noted by K. P. Stanyukovich [1], in addition to root self-similarity, exponential self-similarity is also possible, in which $R = A'e^{mt}$, $\rho_0 = B'e^{nt}$, and $\xi = re^{-mt}/A'$, where A', B', m, and n are constants. The exponential solution satisfies the equation $R\ddot{R}/\dot{R}^2$ = = const when const = 1. In the majority of practically interesting problems, self-similation has an exponential character.

are converted into conditions for functions π, g, and v.

Here we shall write out the system of equations in the common form. The equations will be written subsequently in reference to specific problems. In many motions the scale of density ρ_0 is constant (exponent $\beta = 0$). This takes place, for instance, in all cases when a shock wave (or wave of rarefaction) spreads through an initial gas of constant density.

Exponent β usually differs from zero in those problems in which the density of initial gas is distributed in space by root law of the type $\rho_{00} = \text{const } r^{\delta}$. In these cases exponent β is determined through known exponent δ and α (when $\delta = 0$, $\beta = 0$). Thus, in the system of equations for function π, g, and v (and in boundary conditions) there enters only one new parameter: the exponent of self-similarity α.

The exponents in scale functions in a simple manner are connected with exponents α and β (i.e., α and δ). For instance, when the scale of density is constant ($\beta = 0$, $\rho_0 = \text{const}$), $R \sim t^{\alpha}$, $\dot{R} \sim t^{\alpha-1}$, $P = \rho_0\dot{R}^2 \sim t^{2(\alpha-1)}$.

Inasmuch as the scale of length R in a simple manner is connected with time, the scales of speed, density, and pressure can be considered as functions not of time, but of scale of length R; with help of the relationship $R \sim t^{\alpha}$ we find:

$$\dot{R} \sim t^{\alpha-1} \sim R^{\frac{\alpha-1}{\alpha}}, \quad \rho_0 \sim t^{\beta} \sim R^{\frac{\beta}{\alpha}},$$
$$\Pi \sim \rho_0\dot{R}^2 \sim t^{\beta+2(\alpha-1)} \sim R^{\frac{\beta+2(\alpha-1)}{\alpha}}.$$

From expressions for scale of density $\rho_0 \sim t^{\beta} \sim R^{\beta/\alpha}$ and the law of distribution of initial density in space $\rho_{00} = \text{const } r^{\delta}$, it is clear that $\rho_0 = \rho_{00}(R)$; for instance, as the scale of density ρ_0 serves the initial density of gas at the point where the shock wave is at the time t(R is the coordinate of the front of the shock wave). From this follows the above-mentioned connection of exponents β and δ: $\beta = \alpha\delta$.

When $\beta = 0$, and ρ_0 = const, functions p, ρ, and u by formulas (12.3) can be written in any of the equivalent forms:

$$\left.\begin{aligned} p &= \text{const}\, t^{2(\alpha-1)}\pi(\xi) = \text{const}\, R^{\frac{2(\alpha-1)}{\alpha}}\pi(\xi), \\ u &= \text{const}\, t^{\alpha-1}v(\xi) = \text{const}\, R^{\frac{\alpha-1}{\alpha}}v(\xi), \\ \rho &= \text{const}\, g(\xi). \end{aligned}\right\} \qquad (12.8)$$

§ 3. Conditions of Self-Similarity of Motion

It is natural to pose the question: what requirements must be satisfied by the conditions of a problem so that motion is self-similar? For the answer to this question it follows to draw-on considerations of dimension.

Equations of gas dynamics (12.1) besides variables of functions p, ρ, and u, and independent variables r and t, do not contain any dimensional parameters (the only parameter, γ, is dimensionless). Dimensional parameters enter the initial and boundary conditions of the problem. This also gives the possibility to construct functions p(r, t) and ρ(r, t), since all five variables, p, ρ, u, r, and t, have different dimensions, whereby three of them are independent. Inasmuch as the dimensions of pressure and density contain the symbol of mass, at least one of the parameters of the problem also should contain the symbol of mass.

In many cases this is the constant initial density of gas ρ_0 in $g \cdot cm^{-3}$. In a number of problems the initial density is distributed in space by root law $\rho_{00} = br^{\delta}$. Then this is parameter b, with dimension $[b] = g \cdot cm^{-3-\delta}$. Let us designate the parameter containing the symbol of mass through a. In the most common case its dimension is $[a] = g \cdot cm^k sec^s$. Considering of the dimensions of functions: $[p] = g \cdot cm^{-1} sec^{-2}$, $[\rho] = g \cdot cm^{-3}$, $[u] = cm \cdot sec^{-1}$, it is possible, not disturbing community, to present them in the form proposed by L. I. Sedov [2]:

$$p = \frac{a}{r^{k+1} t^{s+2}} P, \quad \rho = \frac{a}{r^{k+3} t^{s}} G, \quad u = \frac{r}{t} V, \tag{12.9}$$

where P, G, and V are dimensionless functions of independent variables, which depend on dimensionless combinations containing r and t and parameters of the problem.

In the general case there are two dimensionless variables: r/r_0 and t/t_0, where r_0 and t_0 are parameters with dimensions of length and time, either directly enter the conditions of the problem, or can be composed by means of combination of parameters of another dimension. Functions P, G, V then depend on r and t separately and the problem is not self-similar.

It is possible to give a great number of examples of similar motions. Let us refer to one: the problem about a wave of rarefaction which appears when a piston is advanced from a gas with variable speed $u_1 = U(1 - e^{-t/\tau})$ (see § 10, Chapter I). In this example the role of parameter a is played by the constant initial density of the gas ρ_0. Furthermore, the problem contains dimensional parameters $[\tau] = sec$; $[U] = cm \cdot sec^{-1}$, and initial speed of sound $[c_0] = cm \cdot sec^{-1}$ (or initial pressure p_0; $c_0^2 = \gamma \frac{p_0}{\rho_0}$). Dimensionless variables can be, for instance, t/τ and $r/c_0\tau$, or $r/U\tau$ ($r_0 = c_0\tau$ or $U\tau$).

If from the parameters of the problem it is impossible to compose scales of length and time, the variables r and t cannot enter functions P, G, and V separately; the functions can depend only on a dimensionless combination composed from r and t, $\xi = r/At^{\alpha}$, where A is a certain parameter of dimension [A] = cm·sec$^{-\alpha}$. Expressions (12.9) obtain the form

$$p = \frac{a}{r^{k+1} t^{s+2}} P(\xi); \quad \rho = \frac{a}{r^{k+3} t^{s}} G(\xi); \quad u = \frac{r}{t} V(\xi). \tag{12.10}$$

In this case the problem is self-similar and expressions (12.10) are equivalent to expressions (12.3), differing from the latter only by the form of representative functions.

We shall demonstrate this in an example of self-similar motions with constant scale of density. With this, $a = \rho_0$, $k = -3$, $s = 0$, so that expressions (12.10) take on this form:

$$p = \rho_0 \frac{r^2}{t^2} P(\xi), \quad \rho = \rho_0 G(\xi), \quad u = \frac{r}{t} V(\xi). \tag{12.11}$$

Putting here $r = \xi R$ and noticing that $\dot{R} = \alpha R/t$, we find that formulas (12.11) and (12.3) are equivalent if

$$P(\xi) = \alpha^2 \frac{\pi(\xi)}{\xi^2}; \quad G(\xi) = g(\xi); \quad V(\xi) = \alpha \frac{v(\xi)}{\xi}. \tag{12.12}$$

Study of self-similar motions presents great interest. The possibility of reduction of a system of partial differential equations to a system of ordinary differential equations for new representative functions, extraordinarily simplifies the problem from the mathematical standpoint and in a number of cases permits the finding of exact analytic solutions.

Furthermore, frequently self-similar solutions constitute the limits which the solutions of nonself-similar problems asymptotically tend to. Subsequently this position will be clarified in the examination of specific problems.

§ 4. Two Types of Self-Similar Solutions

There exist two sharply different types of self-similar solutions. Solutions of the first type type possess the property that the index of self-similar α, and together with it, the exponents at t or R in all scales, are determined from considerations of dimension or from laws of conservation. The exponents are then fractions with integral numerators and denominators. In problems of this type there always are two parameters with independent dimension. From these parameters there is composed a parameter whose dimension contains the symbol of mass and (see formula (12.10)), and another parameter A, which contains only symbols of length and time. With the help of the second parameter A it is also possible to construct a dimensionless combination, i.e., self-similar variable $\xi = r/At^{\alpha}$. The dimension of parameter A — cm$\cdot$sec^{-a} is determined by the index of self-similarity α. Two motions of such type were considered in Chapter I: the problem about the self-similar wave of rarefaction (§ 11) and the problem about the strong explosion (§25). In the first case the two independent dimensional parameters are initial density and pressure of gas ρ_0 and p_0. From them it is possible to compose a dimensional parameter not containing the symbol of mass: the initial speed of sound $c_0 = (\gamma p_0/\rho_0)^{1/2}$.

The role of parameter A is played by the speed of sound c_0. Correspondingly,

$$\xi = \frac{r}{ct}, \quad \alpha = 1.$$

In the problem concerning the strong explosion, the parameters are initial gas density ρ_0 g$\cdot$cm^{-3} and energy of explosion E g$\cdot$cm$^2\cdot$sec^{-2}, which is always equal to total energy of gas enveloped by motion, owing to which in the problem there appears an integral of energy. (Let us recall that in the problem about the strong explosion the initial pressure and speed of sound p_0, c_0 are assumed to be equal to zero, i.e., these magnitudes are not parameters of the problem). From parameters ρ_0 and E there is composed a parameter not containing mass $A = (E/\rho_0)^{1/5}\text{cm}\cdot\text{sec}^{-2/5}$, so that the self-similar variable is $\xi = r/(E/\rho_0)^{1/5}t^{2/5}$; $\alpha = \frac{2}{5}$.

In an intense explosion in a medium with variable initial density $\rho_{00} = br^{\delta}$, the parameters are the energy of the explosion E $\text{g}\cdot\text{cm}^2\cdot\text{sec}^{-2}$ and coefficient b $\text{g}\cdot\text{cm}^{-3-\delta}$.

From them it is possible to compose parameter A, not containing mass,

$$A = \left(\frac{E}{b}\right)^{\frac{1}{5+\delta}} \text{см}\cdot\text{сек}^{-\frac{2}{5+\delta}}.$$

The self-similar variable has the form

$$\xi = r/\left(\frac{E}{b}\right)^{\frac{1}{5+\delta}} t^{\frac{2}{5+\delta}}; \quad \alpha = \frac{2}{5+\delta}.$$

(A self-similar problem about an explosion in a medium with variable density was considered by L. I. Sedov [2]). A self-similar problem of the same type is the one about propagation of a thermal wave from the place where a definite amount of energy was released (see Chapter X).

As was shown in § 2, the index of self-similarity enters the system of differential equations for representatives as a parameter. Inasmuch as in self-similar problems of the considered type the number α is immediately found from considerations of dimension (or laws of conservation), the matter reduces to integration of the system of equations with known boundary conditions.

In self-similar problems of the second type, exponent α is impossible to find from considerations of dimension or laws of conservation without solution of equations. In this case the actual determination of the index of self-similarity requires integration of ordinary differential equations for representative functions. It turns out that the index is found from the condition that the integral curve passes through a singular point, without which it is not possible to satisfy the boundary conditions.

Examples of self-similar motions of the second type can be the known problems about convergence of a shock wave to the center or about a brief impact, which will be discussed below.

Consideration of solutions of specific problems, belonging to the second type, shows that in all these cases in initial conditions of the problem there is only one dimensional parameter containing the symbol of mass, and there is no second one, with help of which it would have been possible to form parameter A. This also deprives us of the possibility to establish number α with respect to dimension of parameter A. In fact, the problem of course is peculiar to a certain dimensional parameter A $cm \cdot sec^{-\alpha}$; otherwise it would have been impossible to compose the dimensionless combination $\xi = r/At^{\alpha}$. However, the dimension of this parameter (i.e., number α) is not dictated by the initial conditions of the problem, but is found from solution of the equation. The numerical value of parameter A is impossible to find from equations of self-similar motion. It can be determined only by knowing how the given motion appeared. Thus, for instance, if the self-similar motion appeared as a result of some nonself-similar flow, which asymtotically went into a self-similar regime, the magnitude A can be found only be means of numerical solution of the full, nonself-similar problem, when the process of transition of nonself-similar motion to self-similar has been traced. In greater detail these positions will be explained in the examination of specific problems.

Self-similar motions of the first type, in which the index of self-similarity is determined from considerations of dimension, in detail were investigated by L. I. Sedov. Inasmuch as there is already the book of L. I. Sedov [2], in which he gives an exhausting description of these motions and the solution of a number of specific problems, in this chapter we will not remain on self-similar motions of the first type and will be occupied with the study of motions of only the second type.

2. Convergence to the Center of a Spherical Shock Wave and Collapse of Bubbles in a Fluid

§ 5. Formulation of Problem About Convergent Shock Wave

Let us imagine a spherically-symmetric motion in which through a gas of constant initial density ρ_0 and zero pressure to the center of symmetry there goes a strong shock wave. We shall not be concerned with the causes of the appearance of the shock wave. The wave could be created, for instance, by the "spherical piston" which pushed the gas inside, imparting to it some of its energy content. With the convergence of the shock wave to the center there occurs a concentration of energy on the front (cumulation), and the wave is intensified. We shall concern ourselves with the motion of gas at small distances from the center (let us say, small as compared to the initial radius of the "piston"). In moments close to the moment of focusing, and at small radii, the motion, we must assume, to a considerable extent (to what extent will be mentioned below) "forgets" about the initial conditions and emerges into a certain limiting regime which must be found.

In the problem there are no characteristic parameters of length or time. The initial radius of the "piston" cannot serve as the scale for the limiting motion in a region, the dimensions of which are very small as compared to it. The only scale of length is the radius itself of the front of the shock wave R, which is variable in time. The scale of speed is the speed of the front $\frac{dR}{dt} \equiv \dot{R} \equiv D$, which is variable in time. Therefore it is natural to assume that the limiting motion will be self-similar. Earlier, there were no bases for the determination of the index of self-similarity α. Besides initial density ρ_0, there are no other visible parameters, with the help of which it would have been possible to construct a self-similar variable. Certainly, the energy of all the gas, equal to the energy imparted to the gas by the piston, has a fully defined value. However, in a self-similar region, the dimensions of which are small (on the order of R) and decrease with flow of time with convergence of the wave to the center, concentrated only a small, and then decreasing in time, portion of total energy is concentrated.* As will be shown below, the energy in a self-similar region, the radius of which is on the order of R, and mass of the order $\rho_0 R^3$, decreases with the passage of time by root law. However, it decreases when $R \rightarrow 0$ slower than R^3 due to amplification of the shock wave and growth of density of energy (pressure). From what was said it is clear that self-similar motion should belong to the second type. The solution will contain a certain parameter A, of earlier unknown dimension, connected with the index of self-similarity α($[A] = \mathrm{cm}\cdot\mathrm{sec}^{-\alpha}$; see § 2). If the index of self-similarity, i.e., dimension A, is found from the most limiting solution, the numerical value of parameter A will remain indefinite. It depends on the initial conditions of the problem and on the motion of all the gas on the whole.

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*The assumption about the equality to zero of initial pressure, i.e., the fact that the wave is strong, also excludes from problem the parameter of speed, i.e., the initial speed of sound c_0, which together with initial pressure is equal to zero.

As was already mentioned, the limiting, self-simulating solution is valid only in a region of small dimensions of the order of the radius of the front and then near the moment of focusing of the shock wave, when this radius is small.

If we numerically solve the problem about motion of the entire gas on the whole under certain initial conditions ensuring the appearance of a convergent shock wave (the problem with the "spherical piston" accomplishing a shock inside), the true solution in the region with a radius which decreases proportionally to the radius of the front will be even closer to the limiting self-similar solution.

The form of a limiting solution does not depend on the initial conditions and character of motion of the gas at long distances, in particular on the law of motion of the piston.

However, a limiting solution does not completely "forget" about the initial conditions. It "forgets" about the form of initial motion, but selects from all conclusive information, give by the initial conditions, a singular number A, which characterizes the "intensity" of the initial shock (a "stronger" shock corresponds to a large value by A).

If the form of the limiting solution itself does not depend on the initial conditions and motion of the gas at long distances from the center, the character of approximation of the true solution to the limiting one, of course, depends on the initial conditions. The nearer the initial motion is to limiting, the earlier the true motion near the front emerges into a self-similar regime. However, this emergence sooner or latter will certainly occur, no matter what the initial conditions and the motion at long distances are.

Thus, we shall find the self-similar solution of the problem about convergence to the center of a shock wave. This interesting and important problem was solved independently by L. D. Landau and K. P. Stanyukovich [1] and Guderley [3].

§ 6. Fundamental Equations

For the beginning of the reading of time t = 0 we shall take the moment of focusing, when R = 0. Then the time to the moment of focusing turns out to be negative. In connection with this, the determination of the self-similar variable should be changed somewhat, putting

$$R = A(-t)^{\alpha}, \quad \xi = \frac{r}{R} = \frac{r}{A(-t)^{\alpha}}. \tag{12.13}$$

Formally, the solution, that we are seeking envelopes all space, up to infinity, so that the intervals of change of variables are such:

$$-\infty < t < 0; \quad R < r < \infty; \quad 1 < \xi < \infty$$

(actually a self-similar solution is valid only in a region with a radius of the order of R, and at long distances is somehow connected with the solution of a full nonself-similar problem).

On the front of the shock wave $\xi = 1$. The speed of propagation of the front is directed to the center, i.e., it is negative, $D \equiv \dot{R} = \alpha R/t = -\alpha R/|t| < 0$.

We shall place the solution in equations of gas dynamics (12.1) in self-similar form (12.3).

The system reduces to equations (12.4), in which $\nu = 3$, in accordance with the spherical symmetry of motion. The scale of density in the problem is constant, ρ_0 = const (this rather evident affirmation convinces us in the examination of the boundary conditions on the front of the shock wave). Therefore, the member $\dot{\rho}_0/\rho_0$ in the first equation of (12.4) disappears and the bracket returns to zero. The factors, depending on the scales, in equations (12.4) reduce to the following

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constants:

$$\frac{R\ddot{R}}{\dot{R}^2}=\frac{\alpha-1}{\alpha};\quad \frac{R}{\dot{R}}\frac{d}{dt}(\ln \rho_0^{1-\gamma}\dot{R}^2)=\frac{2(\alpha-1)}{\alpha}.$$

We shall obtain a system of equations for the representatives:

$$\left.\begin{aligned}(v-\xi)(\ln g)'+v'+\frac{2v}{\xi}=0,\\ (\alpha-1)\alpha^{-1}v+(v-\xi)v'+g^{-1}\pi'=0,\\ (v-\xi)(\ln \pi g^{-\gamma})'+2(\alpha-1)\alpha^{-1}=0.\end{aligned}\right\}\qquad (12.14)$$

For the purpose of simplification of the system we shall make a series of transformations. Let us turn to the new representative functions P, G, V, connected with the old ones π, g, v by formulas (12.12) (it is possible of course from the very beginning to find the solution of dimensional equations (12.1) in the form of (12.11)). Further, we shall introduce, instead of pressure, a new unknown function, the square of the speed of sound* and correspondingly let us turn to the representative of the square of the speed of sound.

In dimensional variables $c^2 = \gamma p/\rho$. In presentation (12.3) $c^2 = \gamma\dot{R}^2\pi/g = \dot{R}^2 z$, where representative $z = \gamma\pi/g$.

In presentation (12.11), which we crossed to, $c^2 = \gamma\frac{r^2}{t^2}P/G = \frac{r^2}{t^2}Z$, where representative $Z = \gamma P/G$. Formulas (12.12) give the connection between representatives z and Z:

$$Z=\alpha^2\frac{z}{\xi^2}.$$

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*The system of equations of gas dynamics (12.1) can also be written with respect to functions ρ, u, c^2 instead of ρ, u, p:

$$\left.\begin{aligned}\frac{\partial\ln\rho}{\partial t}+u\frac{\partial\ln\rho}{\partial r}+\frac{\partial u}{\partial r}+(\nu-1)\frac{u}{r}=0,\\ \frac{\partial u}{\partial t}+u\frac{\partial u}{\partial r}+\frac{c^2}{\gamma}\frac{\partial\ln\rho}{\partial r}+\frac{1}{\gamma}\frac{\partial c^2}{\partial r}=0,\\ \frac{\partial}{\partial t}\ln c^2\rho^{1-\gamma}+u\frac{\partial}{\partial r}\ln c^2\rho^{1-\gamma}=0.\end{aligned}\right\}\qquad (12.1')$$

After introduction of new variables, system (12.14) obtains the form

$$\begin{gathered}\frac{dV}{d\ln\xi}+(V-\alpha)\frac{d\ln G}{d\ln\xi}=-3V,\\(V-\alpha)\frac{dV}{d\ln\xi}+\frac{Z}{\gamma}\frac{d\ln G}{d\ln\xi}+\frac{1}{\gamma}\frac{dZ}{d\ln\xi}=-\frac{2}{\gamma}Z-V(V-1),\\(\gamma-1)Z\frac{d\ln G}{d\ln\xi}-\frac{dZ}{d\ln\xi}=2\left[\frac{\alpha-1}{\alpha(V-\alpha)}+1\right]Z.\end{gathered}\qquad(12.15)$$

This is a system of three ordinary first order differential equations with respect to three unknown functions V, G, Z from independent variable ξ.

Let us consider the boundary conditions. On the front of the shock wave the laws of conservation are carried out, which in a limiting case of a strong shock wave give known relationships between gas-dynamic magnitudes behind the front and the speed of the front (see formulas in (1.111)):

$$\rho_1=\rho_0\frac{\gamma+1}{\gamma-1};\quad p_1=\frac{2}{\gamma+1}\rho_0D^2;\quad u_1=\frac{2}{\gamma+1}D;\quad c_1^2=\frac{2\gamma(\gamma-1)}{(\gamma+1)^2}D^2.\qquad(12.16)$$

Putting here the expressions of dimensional magnitudes through representatives of (12.11) and considering that on the front of the shock wave $r = R$, $\xi = 1$, and also taking into account that $D = \dot{R} = \alpha R/t$, we obtain the boundary conditions for the representatives: when $\xi = 1$

$$V(1)=\frac{2}{\gamma+1}\alpha;\quad G(1)=\frac{\gamma+1}{\gamma-1};\quad Z(1)=\frac{2\gamma(\gamma-1)}{(\gamma+1)^2}\alpha^2.\qquad(12.17)$$

Hence, one should mention, it is immediately clear that the scale of density does not depend on time or radius of the front. Otherwise it would have been impossible to satisfy the condition $\rho_1 = \frac{\gamma+1}{\gamma-1}\rho_0 = \text{const}$ on the front of the shock wave.

Representatives also obey the conditions to infinity. At the time of focusing t = 0, speed, pressure, and speed of sound at any

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finite radius r are limited. But with $t = 0$ and finite r, $\xi = \infty$. So that with $t = 0$ and final r the magnitude $u = \frac{r}{t}V$, $c^2 = \frac{r^2}{t^2}Z$ are limited, it is necessary that V and Z return to zero. Thus, we obtain another condition, which should satisfy the solution: when $\xi = \infty$

$$V(\infty)=0;\quad Z(\infty)=0. \tag{12.18}$$

In general, the boundary conditions of (12.17) are sufficient in order to begin integration of equations (12.15) from point $\xi = 1$ in the direction of $\xi > 1$, assigning some value of number α.

However the investigation of equations, which will be discussed in the following paragraph, shows that it is impossible to obtain a unique solution and arrive at point (12.18) with an arbitrary value of α. This turns out to be possible only with a certain selected value of α, which also determines the selection of the index of self-similarity.

§ 7. Investigation of Equations

We shall show how the index of self-similarity is found in the solution of equations (12.15). For this purpose it follows first of all to investigate the equations. We shall not adhere to the mathematical strictness of foundations here and give detailed calculations.

We shall only mention the most important fundamental moments, and we shall also outline the basic ways of solving the problem. We shall try to emphasize certain peculiarities of the problem, common either for all self-similar solutions, or for solutions of a second type. Below we shall trace the system of calculation proposed by N. A. Popov, to whom we are thankful for his valuable advice.

Looking at system of equations (12.15) we immediately see that variable ln ξ, which can be considered as a new independent variable instead of ξ, enters the system only in the form of differential d ln ξ. Exactly so, only in the form of differential d ln G, enters one of the unknown functions, i.e., G. This property of equations (12.15), characteristic for any self-similar motions, permits the reduction of the sytem of three differential equations to one differential equation with respect to variables V and Z and two quadratures.* Actually, we shall solve sytem (12.15) with respect to derivatives dV/d ln ξ, d ln G/d ln ξ, dZ/d ln ξ. Instead of writing out the very bulky expressions obtained, we shall write the result of the solution of the algebraic system in symbolic form, through the determinants

$$\frac{dV}{d\ln\xi}=\frac{\Delta_1}{\Delta};\quad \frac{d\ln G}{d\ln\xi}=\frac{\Delta_2}{\Delta};\quad \frac{dZ}{d\ln\xi}=\frac{\Delta_3}{\Delta}. \tag{12.19}$$

where the determinant of system Δ is equal to

$$\Delta=\begin{vmatrix} 1 & V-\alpha & 0 \\ V-\alpha & \frac{Z}{\gamma} & \frac{1}{\gamma} \\ 0 & (\gamma-1)Z & -1 \end{vmatrix}=-Z+(V-\alpha)^2. \tag{12.20}$$

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*The noted property is not random and is a consequence of the dimensional structure of equations of gas dynamics, which do not contain dimensional magnitudes, besides the variables themselves. The fact that some magnitude enters under the differential sign of the logarithm testifies to the arbitrariness in the selection of units for the measurement of this magnitude. Regarding density $\rho = \rho_0 G$, this can be directly seen from equations (12.1'), written for functions ρ, u, c^2 (see footnote on p. 991). If in general nonself-similar equations we change to new independent variables, i.e., $\xi = r|At^{\alpha}$ and $\eta = r/r_0$, where A and r_0 are some externally introduced dimensional parameters, then, inasmuch as the selection of these parameters is not limited to anything, they must be dropped from the equations. And indeed, the transformation shows that the new variables enter the equations only in the form of d ln ξ and d ln η (in the case of self-similar motions all functions depend only on ξ and do not depend on η, so that members d ln η disappear).

Dimensionless values of V and Z are composed from the dimensional variables themselves: $V = t/ru$; $Z = t^2/r^2c^2 = \rho t^2/r^2\gamma p$, without the participation of any outside parameters; therefore, in the equations they enter in free form, not under the sign of d ln.

Determinants Δ_1, Δ_2, Δ_3 are obtained after replacement of corresponding columns in determinant (12.20) by the right parts of equations (12.15).

Coefficients with derivatives and right sides in equations (12.15) depend only on V and Z, but do not depend on G and ξ, so that all magnitudes Δ, Δ_1, Δ_2, Δ_3 are functions only of V and Z. Dividing the third and the first equation by (12.19) into each other, we obtain an ordinary first order differential equation:

$$\frac{dZ}{dV}=\frac{\Delta_3(Z, V)}{\Delta_1(Z, V)}. \qquad (12.21)$$

After we find the solution of this equation Z(V), it can be placed in the first equation by (12.19) and by means of quadrature we can determine the function $V(\xi)$, and then, putting $V(\xi)$ and $Z[V(\xi)]$ in the second equation, by means of quadrature we can find the function $G(\xi)$.

In fact, one quadrature is enough, since the system of equations (12.15) possesses one integral, which is the algebraic relationship between all variables. The existence of this integral, the integral of adiabaticity, is connected with the fulfillment of the law of conservation of entropy in a gas particle.* In general, fulfillment

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*In order to derive the integral of adiabaticity, we shall use the first and third equations of (12.15). The first (equation of continuity) will be divided by $V - \alpha$ and will be presented in the form

$$d\ln G+d\ln(V-\alpha)=-3d\ln\xi-\frac{3\alpha d\ln\xi}{V-\alpha}.$$

The third (entropy) equation will be divided by Z and will be presented in the form

$$d\ln G^{\gamma-1}Z^{-1}=\frac{2(\alpha-1)\alpha^{-1}d\ln\xi}{V-\alpha}+2d\ln\xi.$$

Excluding $d \ln \xi/(V - \alpha)$ from these two equations and grouping all members to one side, we obtain an equation of the form $d \ln \{\xi, G, V, Z\} = 0$, which gives integral $\{\xi, G, V, Z\} = \text{const}$. The constant is determined with the help of boundary condition (12.17).

of laws of conservation always is accompanied by the existence of corresponding integrals of self-similar equations. Thus, in the problem about the strong explosion (see § 25, Chapter I) the equations possess an integral of energy.

Thus, the basic problem reduces to the solution of equation (12.21) with boundary conditions (2.17) and (2.18).

Let us consider how the unknown integral curve passes on plane VZ. On the front of a shock wave when $\xi = 1$, $V = V(1)$ and $Z = Z(1)$ (see formulas (2.17)). Let us plot this point on a plane and designate it by the letter Φ. To infinity, when $\xi = \infty$, $V(\infty) = 0$ and $Z(\infty) = 0$, i.e., integral curve $Z(V)$ goes from point Φ to the origin of coordinates O (Fig. 12.1).

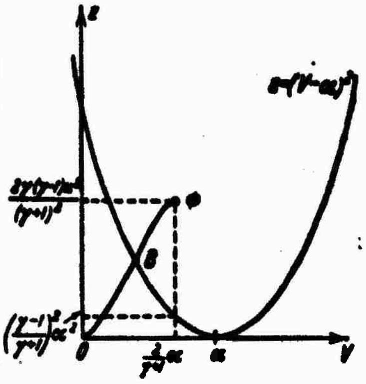

Fig. 12.1. Shape of integral curve on plane V, Z.

So that the solution of equations of gas dynamics has a physical meaning, it should be simple. Every value of independent variable ξ must correspond to the singular values of V and Z. This means that functions ξ of V and ξ of Z or, all the same, $\ln \xi$ of V and $\ln \xi$ of Z, should not have extrema. Derivatives $d \ln \xi/dV = \Delta/\Delta_1$ and $d \ln \xi/dZ = \Delta/\Delta_3$ in the region of variation of variable $1 < \xi < \infty$, $0 < \ln \xi < \infty$ in a true solution nowhere should return to zero.

But determinant $\Delta = -Z + (V - \alpha)^2$ is equal to zero on parabola $Z = (V - \alpha)^2$, drawn on plane VZ (Fig. 12.1). It is easy to check by means of direct calculation that point Φ lies higher than the parabola, i.e., the unknown integral curve along its path from point Φ to point O by means should intersect the parabola. So that the derivatives $d \ln \xi/dV$ and $d \ln \xi/dZ$ do not return to zero, it is necessary that at the point of intersection the determinants Δ_1 and Δ_3 return to zero (it is possible to check that when $\Delta = 0$, Δ_1 and Δ_3 return to zero simultaneously). Thus, the point of intersection of the true integral curve Z(V) and the parabola is the singular point of equation (12.21) ($\Delta_1 = 0$, $\Delta_3 = 0$, $dZ/dV = 0/0$).

If one were to assign some arbitrary value of the index of self-similarity α, and start to integrate equation (12.21) from point Φ, the integral curve either in general will not intersect the parabola, or will intersect it in some ordinary point, and this curve will not respond to the true solution.

Only at a special, selected value of α will the integral curve intersect the parabola, passing through the necessary singular point of equation (12.21), and tend to its final point 0. This condition of obligatory passage of the true integral curve through a defined singular point of equation (12.21) is also determined by index α. Singular point B and the schematic trend of a true integral curve are shown in Fig. 12.1 (it is possible to show that point B lies on the left branch of the parabola).

In singular point B, through which there passes the true integral curve Z(V), magnitudes Z and V take definite values that are connected, in addition, to the equation of the parabola $Z = (V - \alpha)^2$. Inasmuch as V and Z are functions of ξ, the singular point corresponds to the definite value of $\xi = \xi_0$. In turn, the value of $\xi = \xi_0$ corresponds to a certain line on plane r, t, the "ξ_0-line." The equation of this line is $r = R(t)\xi_0 = A(-t)^\alpha\xi_0$, and the differential equation for it has the form of $dr/dt = \dot{R}\xi_0$.

The line of the front of a shock wave is: $\xi = 1$, $r = R(t)$, $\frac{dr}{dt} = \dot{R}$. Both lines are shown in Fig. 12.2 (let us note that axis r is line $\xi = \infty$).

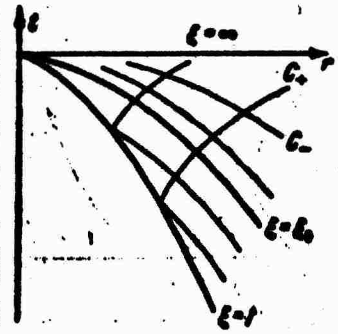

Fig. 12.2. r, t-diagram for the process of convergence of a shock wave to the center. $\xi = 1$ — line of front of shock wave, $\xi = \xi_0$ - ξ_0-line. Several characteristics of the C_+- and C_--sets have been plotted.

The ξ_0-line possesses an important property; it is one of C_--characteristics. In order to be convinced in this, we shall turn in the dimensional equation for C_--characteristics $dr/dt = u - c$ to self-similar variables. Here one should consider that the speed of sound c is a magnitude that is essentially positive. Its accepted scale $\dot{R}$ or r/t is negative. Consequently, when extracting the root from expression $c^2 = \frac{r^2}{t^2} Z$ one should put $c = -\frac{r}{t}|\sqrt{Z}|$.

Thus,

$$\frac{dr}{dt} = u - c = \frac{r}{t}V + \frac{r}{t}|\sqrt{Z}| = \frac{R}{t}\xi(V + |\sqrt{Z}|) = \frac{\dot{R}\xi}{\alpha}(V + |\sqrt{Z}|).$$

We shall be concerned with those C_--characteristics which pass through the ξ_0-line on plane r, t. For this we shall put $\xi = \xi_0$ in the equation of characteristics. But when $\xi = \xi_0$

$$Z(\xi_0) = [V(\xi_0) - \alpha]^2, \quad |\sqrt{Z(\xi_0)}| = \alpha - V(\xi_0)$$

(since $V < \alpha$. Actually, when $\xi = 1 V(1) = \frac{2}{\gamma + 1}\alpha < \alpha$; when $\xi = \infty, V = 0$; function $V(\xi)$ is monotonic). Therefore the considered C_--characteristics in every point of the ξ_0-line have slope $\frac{dr}{dt} = \frac{\dot{R}\xi_0}{\alpha}[V(\xi_0) + |\sqrt{Z(\xi_0)}|] = \dot{R}\xi_0$, which coincides with the slope of the ξ_0-line itself. This means that the ξ_0-line either envelopes the set of C_--characteristics, or simply coincides with one of them. It turns out that the second statement is valid: ξ_0-line coincides with the C_--characteristic, i.e., it is the C_--characteristic itself.

From this follows an important result, concerning the casual relationship of phenomena. As it is known, in a region of continuous flow the characteristics of one set never intersect. This means that

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all those C_--characteristics which pass above the ξ_0-line (see Fig. 12.2) do not overtake the front of the shock wave until the moment of focusing. (C_--characteristics, passing below the ξ_0-line, overtake the front; C_+-characteristics themselves emerge from the line of the front).

Thus, the ξ_0-line limits the region of influence. The state of motion in a given moment of time in those points which lie to the right of the ξ_0-line, i.e., at distances r, greater than $r_0 = R(t)\xi_0$, in no way will influence the motion of the shock wave.

The above-noted properties of the solution; passage of true integral curve through a singular point, possible only at a selected value of the index of self-similarity α (from where this value is also determined), and the existence of the ξ_0-line on plane r, t, which corresponds to a singular point, is a characteristic and limits the region of influence, i.e., are peculiar to all self-similar regimes of the second type.

§ 8. Results of Solution

Practically, the solution and index of self-similarity is found by the trial and error method. Assigning some value of α, we numerically integrate equation (12.21) from initial point Φ ($\xi = 1$) and check how the integral curve proceeds. Correcting the value of α, by means of series approximations we try to obtain that the integral curve intersects the parabola in the needed singular point and tends to final point O. L. D. Landau and K. P. Stanyukovich [1] indicated a method of approximation with the help of which there can be found the value of α, very close to the actual value. This value was used for the first attempt and then definitized. After index α and function Z(V) are found, the finding of functions $V(\xi)$, $Z(\xi)$, $G(\xi)$ is not difficult.

In such a way in works [1, 3] there was found the value of the index of self-similarity $\alpha = 0.717$ for adiabatic exponent $\gamma = 7/5$. Furthermore, in [1] it was found that $\alpha = 0.638$ for $\gamma = 3$, and it was also established that in the limit of $\gamma \to 1$, $\alpha \to 1$. Laws of change of radius and speed of the front of a shock wave, and also pressure behind the front when $\gamma = 7/5$ are such:

$$R \sim |t|^{\alpha} \sim |t|^{0{,}717},$$

$$|\dot{R}| \sim |t|^{\alpha-1} \sim R^{\frac{\alpha-1}{\alpha}} \sim |t|^{-0{,}283} \sim R^{-0{,}395},$$

$$p_1 \sim |t|^{2(\alpha-1)} \sim R^{\frac{2(\alpha-1)}{\alpha}} \sim |t|^{-0{,}566} \sim R^{-0{,}79}.$$

Distribution of speed u and pressure p along the radius in various moments of time when $\gamma = 7/5$ are shown in Fig. 12.3, taken from the book by K. P. Stanyukovich [1]. Speed behind the front monotonically drops, pressure at first increases somewhat, and then also drops.* Density behind the front monotonically increases.

A shock wave continuously accelerates and amplifies upon convergence to the center. When $t \to 0$ and $R \to 0$ pressure and temperature on the front tend to infinity; gas density remains finite; on the front of wave it is constant and is equal to $[\gamma + 1)/(\gamma - 1)]\ \rho_0$.

Upon convergence of the shock wave there occurs a concentration of energy near the front of the shock wave: temperature and pressure increase without limit. However, due to the fact that the actual dimensions of a self-similar region decrease in time, the total energy concentrated in it also decreases. A self-similar solution is valid only in a certain sphere, whose radius decreases together with the

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*Such a pressure trend is not common; for instance, when $\gamma = 3$ the pressure, as also speed, monotonically decreases behind the front of a shock wave.

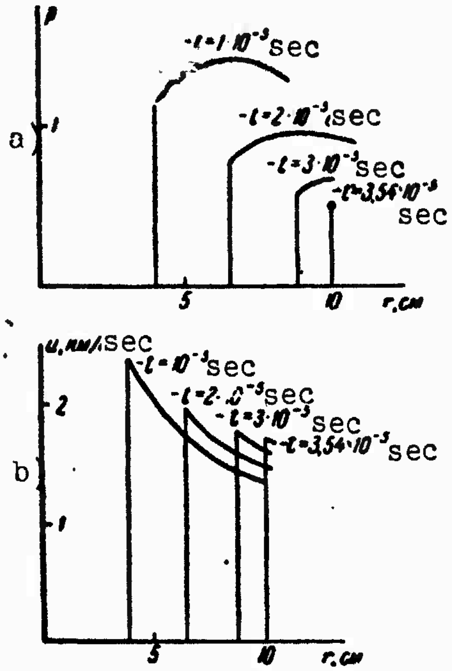

Fig. 12.3. Distribution of pressure in arbitrary units (a) and speed (b) in various moments of time upon convergence of a shock wave to the center, $\gamma = 7/5$. Graphs are taken from book [1].

radius of the front, in proportion to R, i.e., the effective boundary of the self-similar region is a certain constant value of $r/R = \xi = \xi_1$. The amount of energy enclosed in the self-similar region, i.e., in a sphere of variable radius $r_1 = \xi_1 R$, is equal to:

$$E_{\text{авт}} = \int_R^{r_1} 4\pi r^2\, dr \rho \left(\frac{1}{\gamma - 1} \frac{p}{\rho} + \frac{u^2}{2} \right) =$$

$$= 4\pi R^3 \rho_0 \dot{R}^2 \int_1^{\xi_1} g \left(\frac{1}{\gamma - 1} \frac{\pi}{g} + \frac{v^2}{2} \right) \xi^2\, d\xi.$$

The integral with respect to ξ from 1 to ξ_1 is a constant number, so that energy $E_{\text{self}} \sim R^3 \dot{R}^2 \sim R^{5-(2/\alpha)}$.

For all real values of adiabatic exponent γ the power of R is positive. For instance, when $\gamma = 7/5$ $\alpha = 0.717$

$$E_{\text{авт}} \sim R^{2.21} \to 0 \text{ when } R \to 0.$$

If one continues integration of ξ ad infinitum ($\xi_1 = \infty$), the integral diverges. (This is clarified in the footnote on p.1002). Thus, the energy in the whole space within the confines of the self-similar solution is infinite. This in particular also confirms the inapplicability of the self-similar solution to large radii r (at given radius of front R).

The amount of energy enclosed in a sphere of constant radius r can increase (but not infinitely); however, motion in all the region from R to r = const > R is not described by a self-similar solution. The self-similar solution pertains only to the entire decreasing sphere $r_1 \sim R$, $\xi_1 \approx$ const, whereas $\xi = \frac{r}{R} \to \infty$ when $r =$ const and $R \to 0$.

The form of limiting distributions of gas-dynamic magnitudes with respect to radius at the time of focusing $t = 0$ can be established on the basis of considerations of dimension. At our disposal there is only one parameter A cm·sec$^{-\alpha}$, with the help of which it is possible to connect speed u and speed of sound c with radius r.

This gives a limiting law at the time $t = 0$:

$$u \sim c \sim A^{\frac{1}{\alpha}} r^{1-\frac{1}{\alpha}} = A^{\frac{1}{\alpha}} r^{-\frac{(1-\alpha)}{\alpha}}.$$

Inasmuch as moment $t = 0$ and $r \neq 0$ corresponds to the value of $\xi = \infty$, limiting density $\rho = \rho_0 G(\infty)$ is constant with respect to radius. Limiting distribution of pressure consequently is

$$p = \frac{1}{\gamma} \rho c^2 \sim \rho_0 A^{\frac{2}{\alpha}} r^{-\frac{2(1-\alpha)}{\alpha}}.$$

Limiting laws $u(r)$, $c(r)$, and $p(r)$ naturally coincide with the laws on the front in the course of the process of $u_1(R)$, $c_1(R)$, and $p_1(R)$ (with an accuracy of numerical coefficients).*

The numerical coefficients in the limiting laws for $u(r)$, $c(r)$, and $p(r)$, just as the limiting value of density $\rho_{\text{limit}} = \rho_0 G(\infty)$, can

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*Limiting laws can also be established analytically, proceeding from equations for representatives, if one finds the asymptotic solution in the vicinity of point $\xi = \infty$, $V = 0$, and $Z = 0$. We shall obtain: $V \sim \xi^{-1/\alpha}$, $Z \sim \xi^{-2/\alpha}$, which upon transition to dimensional magnitudes will also give the limiting laws described in the text. Magnitudes v^2 and $z = \gamma\pi/g$ when $\xi \to \infty$ according to determination (12.12) are proportional to $v^2 \sim z \sim \xi^2 V^2 \sim \xi^{2-\frac{2}{\alpha}}$; $g(\infty) = G(\infty) =$ const. Hence it is clear that the integral of energy diverges when $\xi_1 \to \infty$

$$\int_{1}^{\xi_1} g\left(\frac{1}{\gamma-1}\frac{\pi}{g} + \frac{v^2}{2}\right)\xi^2 d\xi \sim \int_{1}^{\xi_1} \xi^{4-\frac{2}{\alpha}} d\xi \sim \xi_1^{5-\frac{2}{\alpha}} \to \infty,$$

and the energy in the whole space within the confines of the self-similar solution is infinite in any moment of time.

be found only as a result of the solution of equations of self-similar motion. When $\gamma = 7/5$ limiting density is equal to $\rho_{limit} = 21.6\rho_0$ (density on the front of the shock wave is $\rho_1 = 6\rho_0$). The same value of $\rho = 12.6\rho_0$ is possessed by density at large distances from the front $r \to \infty$ and up to the moment of focusing (since when $R \neq 0$ and $r \to \infty$, $\xi = r/R \to \infty$) and $\frac{\rho}{\rho_0} = G(\xi) \to G(\infty)$.

The energy of content, concentrated in a sphere of radius r at the time of focusing, is proportional to

$$\int_0^r 4\pi r^2 dr \rho \left(\frac{1}{\gamma-1}\frac{p}{\rho} + \frac{u^2}{2}\right) \sim r^{5-\frac{2}{\alpha}}$$

(just as $E_{self} \sim R^{5-\frac{2}{\alpha}}$; see above).

The energy concentrated in a sphere of finite radius is finite, and when $r \to 0$ it also tends to zero. The greater the sphere, the greater the amount of energy included in it (within the confines of the self-similar regime).

After the moment of focusing, when $t > 0$, reflected from the center, the shock wave spreads through the gas, moving toward it, to the center. The motion in this stage is also self-similar and the index of self-similarity does not change. The law of propagation of the front of a reflected shock wave when $t > 0$ is $R \sim t^{\alpha}$.

Calculations show that when $\gamma = 7/5$ the density of gas behind the front of a reflected shock wave is equal to $\rho_{1\ ref} = 137.5\rho_0$, and it is 23 times more than the density behind the front of the incident wave, $\rho_1 = 6\rho_0$. The speed behind the front is positive, i.e., the gas scatters from the center, where the speed of scattering decreases in time, starting from infinity, in accordance with the laws $R \sim t^{\alpha}$ and

$R \sim t^{-(1-\alpha)}$.*

§ 9. Collapse of Bubbles. Rayleigh Problem

With the process of convergence of a shock wave to the center there is a large number of common lines in the process of collapse of bubbles in a fluid (in water). In a real fluid there frequently form little bubbles filled by the vapor of the fluid and undissolved gases. The phenomenon of formation of bubbles carries the name of cavitation. In stationary conditions a bubble is stable and gas pressure from within balances the pressure in the fluid. When the fluid participates in the motion and goes from a region of low pressure to a region of higher, internal pressure in a bubble which was formed earlier, at low pressure, and becomes less than the new high pressure in the fluid. The fluid then runs to the center, collapsing the bubble. When collapsing a bubble, as also when focusing a shock wave, there occurs concentration of energy. The speeds of collapse and pressure grow with the decrease of radius of the bubble and in the focusing stage attain very large values. After collapse, in the central region there will form a pressure peak and from the center spreads a shock wave.

When a similar process occurs near solid surfaces, a shock wave

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*In the work of one of the authors of [26] there is constructed a set of self-similar solutions for cylindrical motion in the acoustic approach. It is obtained by means of superposition of plane waves. The index of self-similarity is arbitrary and is selected according to the initial conditions. For a convergent cylindrical shock wave (in the acoustic approach) pressure on the front $p \sim |t|^{-1/2}$, where radius of the front is $R = c|t|$.

It is interesting that in a reflected shock wave the pressure on ~~the~~ front is infinite when $R \neq 0$. The results for the shock wave were obtained earlier by Ye. I. Zababakhin and M. N. Nechayev [27]. Pressure on the front returns to infinity only within the confines ~~of the~~ acoustic, which is explained in [26].

can lead to damages to the material of the surfaces. It is considered that this is one of the causes of fast wear of screw propellers and turbines.

The problem about the motion of a fluid during the collapse of a bubble in an idealized setting was solved by Rayleigh [4]. The fluid was considered to be ideal (inviscid) and incompressible. The spherically symmetric cavity was considered to be empty, i.e., pressure inside and on the surface of the cavity was assumed equal to zero.*

Let us assume that in the initial moment there is a spherical cavity with radius R_0 in a fluid. Pressure in the surrounding fluid is equal to p_0, and the fluid rests. Distribution of speed along radius r, after the beginning of motion, will be found from a continuity equation when ρ = const:

$$u=\dot{R}\frac{R^2}{r^2}=\dot{R}\frac{1}{\xi^2},\quad \xi=\frac{r}{R}, \tag{12.22}$$

where R(t) is the radius of the cavity and $\dot{R}$ is the boundary speed. Putting the expression for speed in the equation of motion and integrating it with respect to r from r to ∞, we obtain the distribution of pressure:

$$p=p_0+\varrho\frac{\ddot{R}R+2\dot{R}^2}{\xi}-\varrho\frac{\dot{R}^2}{2\xi^4}. \tag{12.23}$$

If we carry this equation to the boundary of the cavity $\xi = 1$, where p = 0, we shall obtain an equation for function R(t):

$$0=p_0+\varrho\left(\ddot{R}R+\frac{3}{2}\dot{R}^2\right). \tag{12.24}$$

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*Obviously, in a real process on the last stage of collapse, the pressure of vapors inside increases so much that it restrains the pressure of the fluid and forces it to recede. Owing to very fast compression, the vapor does not condense and its compression at the end occurs according to Poisson's adiabat. However, considering collapse up to not too small radii, vapor pressure can be disregarded. It is also possible to disregard surface tension on the fluid boundary.

Integrating the equation once with initial condition $\dot{R} = 0$ when $R = R_0$, we obtain the law of build-up of speed during collapse:

$$\dot{R}^2 = \frac{2p_0}{3\rho}\left(\frac{R_0^3}{R^3} - 1\right)^{*)}. \tag{12.25}$$

This equation can also be obtained directly from energy considerations. Let us take as zero the energy of the fluid without a bubble. Potential energy of the fluid, which has a bubble of radius R, is equal to the work expended in surmounting the forces of external pressure in a cavitation with volume $4\pi R^3/3$. This work is equal to $p_0 4\pi R^3/3$, independently of distribution of pressure in the region of the bubble.**

Kinetic energy of the fluid is equal to

$$\int_R^\infty 4\pi r^2 \frac{\rho u^2}{2}\, dr = \int_R^\infty 4\pi r^2 \rho \frac{\dot{R}^2 R^4}{2r^4}\, dr = 2\pi\rho \dot{R}^2 R^3.$$

Total energy, equal to the sum of kinetic and potential, is retained:

$$2\pi\rho\dot{R}^2 R^3 + \frac{p_0 4\pi R^3}{3} = E = \frac{p_0 4\pi R_0^3}{3}. \tag{12.26}$$

Hence we obtain expression (12.25).

With the help of relationship (12.24) the profile of pressure (12.23) can be presented in the form

$$p = p_0\left(1 - \frac{1}{\xi}\right) + \frac{\rho\dot{R}^2}{2}\left(\frac{1}{\xi} - \frac{1}{\xi^4}\right), \quad \xi = \frac{r}{R}.$$

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*Integration of equation (12.25) gives the collapse time of the bubble $\tau = 0.915\, R_0\sqrt{\rho/p_0}$. For instance, in water when $\rho = 1$ g/cm^3, $p_0 = 1$ atm, $R_0 = 1$ mm, $\tau = 0.915 \cdot 10^{-4}$ sec.

**It is possible to explain this position in the following way. Let us imagine a vessel with a fluid, located under pressure p_0, closed by a moving piston with surface area S. If inside there forms a cavity with volume Ω, the fluid, by virtue of its incompressibility, presses the piston at distance l, such that $lS = \Omega$. It then performs on the piston the work of $p_0 Sl = p_0\Omega$, which is determined only by pressure p_0 far off from the bubble and does not depend on distribution of pressure near the bubble.

(profiles of speed and pressure are schematically depicted in Fig. 12.4.)

From the formula for pressure it is clear that the problem is not self-similar (in spite of the "self-similar" form of speed (12.22)). This is understandable: the problem has characteristic scales of length R_0 and speed $\sqrt{p_0/\rho}$.

However, in the limit when the radius of the cavity tends to zero, $R \rightarrow 0$, and speed and pressure grow, tending to infinity, and the solution asymptotically takes on a self-similar character:

$$p \approx \frac{\rho \dot{R}^2}{2}\left(\frac{1}{\xi}-\frac{1}{\xi^4}\right); \quad \dot{R}^2 \approx \frac{2p_0}{3\rho}\frac{R_0^3}{R^3}. \tag{12.27}$$

The scale of length, the initial radius, becomes too large, and the scale of pressure p_0 becomes too small to characterize a ture process, for which the cavity radius R and boundary $\dot{R}$ now serve as the scales ($R \ll R_0$; $\dot{R} \gg \gg \sqrt{\frac{p_0}{\rho}}$; $p \sim \rho\dot{R}^2 \gg p_0$). The motion as if "forgets" about the initial conditions. This in particular is seen in the fact that parameters p_0 and R_0 now enter the equation of motion of the boundary not separately, as earlier (see formula (12.25)), but only in a combination, proportional to the total energy of fluid $E = 4\pi R_0^3 p_0/3$ (see formula (12.27)).

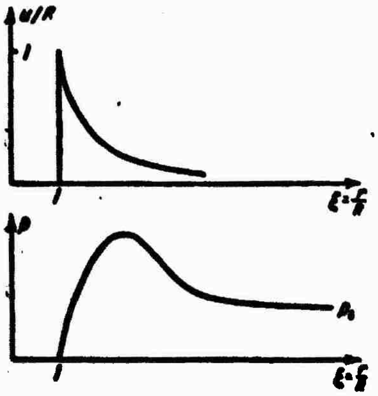

Fig. 12.4. Profiles of speed and pressure in the Rayleigh problem.

As we see, self-similarity belongs to the first type, i.e., the energy is retained. The dimensional parameters in the self-similar flow are the same as in the problem about the strong explosion, i.e., energy and density. The law of boundary motion is given by equation (12.27) $\dot{R}^2 \sim \frac{E}{\rho}\frac{1}{R^3}$, and pressure $p \sim E/R^3$. Hence we immediately obtain $R \sim (E/\rho)^{1/5}(-t)^{2/5}$; $\dot{R} \sim (E/\rho)^{1/5}(-t)^{-3/5}$, as in the problem about the strong explosion (the moment of focusing is taken as zero). Index of self-similarity is $\alpha = 2/5$.

In the limit $R \to 0$ from formulas (12.22) and (12.27) we obtain

$$u \sim \dot{R}\frac{R^2}{r^2} \sim \frac{R^{\frac{1}{2}}}{r^2}; \quad p \sim \frac{1}{R^3}\left(\frac{R}{r} - \frac{R^4}{r^4}\right) \sim \frac{1}{R^2 r} - \frac{R}{r^4}.$$

Boundary speed tends to infinity, $\dot{R} \sim R^{-3/2}$, but speed on finite radius $r \neq 0$ tends to zero. In the limit $R \to 0$ the potential energy $p_0 4\pi R^3/3$ tends to zero, and all energy E, which is new kinetic, is concentrated at the point of origin of the coordinates. Energy density in it is infinite. In distinction from speed, the pressure at the time of focusing is infinite at any finite radius $r \neq 0$ (energy is not connected with pressure in the model of incompressible fluid). This testifies to the imperfection of the model of incompressible fluid. As will be shown in the following paragraph, in the calculation of compressibility the pressure at finite distances from the center is limited.

§ 10. Collapse of Bubbles. Calculation of Compressibility and Viscosity

Collapse of an empty cavity in water, taking into account compressibility (but without taking into account viscosity), was considered by Hunter [5]. The equation of state was adopted in form of

$$p = B\left[\left(\frac{\rho}{\rho_0}\right)^{\gamma} - 1\right]$$

with $\gamma = 7$. However, actually, in the limit of large pressures the unit was lowered, so that the equation of state had a form analogous to the gas type, $p = B(\rho/\rho_0)\gamma$. Magnitude B was assumed to be constant, not depending on entropy (flow was considered to be isentropic). It was taken that $B = 3000$ atm.

Numerical solution of equations of hydrodynamics (in variables u, c) with properly selected initial and boundary conditions showed that in the limit when the radius of the cavity becomes very little, and boundary speed is very great, the solution becomes self-similar.

In accordance with this, we found the solution of the equations in self-similar form $u = \dot{R}v(r/R)$, $c^2 = \dot{R}^2 z(r/R)$, where the radius of the cavity is $R = A(-t)^{\alpha}$.* Equations in self-similar variables, their general properties, and the course of the investigation in many respects are analogous to what takes place in the problem about convergence of a shock wave to the center. As a result of numerical integration the index of self-similarity α was equal to $\alpha = 0.555$ (for $\gamma = 7$).

The energy of the entire flow is infinite, as in the problem about focusing of a shock wave. (Energy enclosed in a sphere with radius r at the time of focusing $t = 0$, $R = 0$, is proportional to $r^{1.13}$). The absence of an integral energy also refers the self-similar problem to the second type. Distributions of speed, square of the speed of sound, and density along the radius at the time of collapse of the cavity, when $R = 0$, have the form

$$u \sim r^{-\frac{1-\alpha}{\alpha}}; \quad c^2 \sim r^{-\frac{2(1-\alpha)}{\alpha}}; \quad \varrho \sim r^{-\frac{2(1-\alpha)}{\alpha(\gamma-1)}}; \quad p \sim r^{-\frac{2(1-\alpha)\gamma}{\alpha(\gamma-1)}}.$$

In distinction from the case of focusing a shock wave, when distributions u and $c^2 \left(c^2 \sim \frac{p}{\rho}\right)$ have the same form, the limiting density here is variable. This is connected with the fact that from the very beginning the problem is considered to be isentropic. A sharp increase of c^2 and p is not connected with the growth of entropy,

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*For investigation and solution of the equations it turned out to be more convenient to select as a self-similar variable not $\xi = r/R = r/A(-t)^{\alpha}$, but the magnitude $\xi' = -(R/r)^{1/\alpha} = A^{1/\alpha} t r^{-1/\alpha}$ (on the boundary of the cavity $r = R$, $\xi' = -1$; to infinity $r = \infty$, $\xi = 0$).

as in a shock wave, but with the growth of density.

The self-similar solution in some measure describes the real process only in the region of very small radii, when the intial conditions are "forgotten."

A comparison of the self-similar solution with the results of numerical integration of partial differential equations at initial conditions, corresponding to atmospheric pressure in water and initial radius $R_0 = 0.5$ cm, showed the following. At the time of full collapse $t = 0$, $R = 0$ the self-similar solution is valid in the region with radius of the order 10^{-2} cm. Such a sphere contains approximately 10-20% of the fluid energy, and the pressure on its boundary is of the order of several tens of thousand atmospheres. In the work of Hunter there is also found a self-similar solution for a shock wave which spreads from the center after bubble collapse.

The calculation of viscosity of a fluid leads to interesting regularities. The problem about collapse of an empty spherical cavity in an incompressible viscous fluid was solved by Ye. I. Zababakhin [6].

Investigation of equations indicate that the character of motion depends on Reynolds number $Re = \frac{R_0}{\nu}\sqrt{\frac{p_0}{\rho}}$, where $\nu = \eta/\rho$ is the kinematic viscosity. When $Re > Re$,* where Re* is a certain critical number (low viscosity), the boundary speed of the cavity $\dot{R}$ increases without limit when $R \to 0$ by the same law as in the Rayleigh problem, $\dot{R} \sim R^{-3/2}$, but with a smaller value of the proportionality factor (part of the energy is turned into heat at the expense of dissipation). When $Re < < Re^*$ (high viscosity) the viscosity strongly prevents acceleration of the fluid, and bubble collapse occurs slowly, in an infinite length of time. Cumulation of energy, characteristic for the Rayleigh problem, is absent. In an intermediate case when $Re = Re^*$ the bubble collapses in a finite length of time; speed $\dot{R}$ when $R \to 0$ grows without limit, but weaker than R^{-1}.

Numerical integration of equations for critical Reynolds number gives the value of $Re^* = 8.4$. For a given fluid, under a given pressure, i.e., at assigned ρ, ν, p_0, it is possible to speak of the critical radius of the bubble R_0^*. When $R_0 < R_0^*$ cumulation is completely removed by viscosity. Practically, the critical radius is extraordinarily small; for instance, in water ($\rho = 1$ g/cm^3, $p_0 = 1$ atm, and $\nu = 0.01$ cm^2/sec) $R_0^* = 0.8 \cdot 10^{-4}$ cm.

Consequently, viscosity weakly affects the collapse of bubbles with radius exceeding $0.8 \cdot 10^{-4}$ cm.

3. Emergence of a Shock Wave on the Surface of a Star

§ 11. Propagation of a Shock Wave Following the Root Law of Decrease of Density

We know (see for example [7]) that near the surface of a star the density of matter drops to zero approximately by root law

$$\rho_{00} = b x^{\delta}, \tag{12.28}$$

where x is the coordinate which is counted off from the surface inside the star, and b and δ are constants. Such distribution of density is established as a result of the joint action of forces of gravitation and thermal pressure, whereby in the establishment of distribution of temperature, which is proportional to the pressure of gas, an essential role is played by radiant thermal conduction (see also § 14, Chapter II). Exponent δ in the distribution of density (12.28) is connected with the constants entering the law of radiant thermal conduction; it is usually on the order of 3.

When in the central regions of a star there occur internal perturbations accompanied by an increase of pressure, there will form a shock wave, which spreads from the central regions to the periphery and emerges on the surface. Propagation of the shock wave through gas with density falling to zero, as this takes place near the surface, is accompanied by a concentration (cumulation) of energy, which is of great interest to astrophysics and to the problem of the appearance of cosmic rays (see following paragraph).

There is a certain physical similarity between the processes of cumulation during propagation of a shock wave through a gas with density falling to zero and during convergence of a shock wave in the center. In both cases the energy is impart without limit to the decreasing mass of substance in such a way that the specific energy, i.e., the energy of a unit of mass, grows without limit. The distinction consists of the causes of decrease of mass, to which the energy drops. In the first case the mass decreases due to the decrease of density of the gas and in second, due to the decrease of volume.

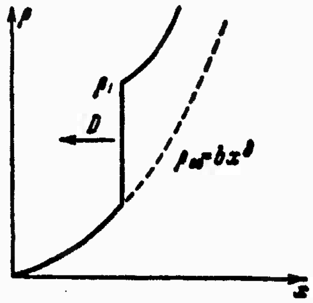

Fig. 12.5. Diagram of emergence of a shock wave on the surface of a star. Density profile.

We shall be concerned with a limiting form of motion in that stage, when the front of the shock wave is close to the surface of a star. In these conditions it is possible to disregard the curvature of surfaces of the star and the front and to consider the motion to be plane. Inasmuch as the shock wave is strong, it is possible to disregard the forces of gravitation. Radiant thermal conduction plays an essential role in the establishment of stationary distributions of temperature of gas density. In the short time of passage of a very strong shock wave, it does not succeed in introducing noticeable changes at the expense of redistribution of heat; therefore, the process can approximately be considered as adiabatic.

In such a formulation the problem about the limiting form of motion was for the first time solved by G. M. Gandel'man and D. A. Frank-Kamenetskiy [8]. The same problem was later considered by Sakurai [9], who found exactly the same solution, but for other numerical values of exponent δ in law (12.28) and adiabat γ. A schematic representation of the process of propagation of a shock wave is shown in Fig. 12.5.

The single dimensional parameter in conditions of the problem is constant b, which contains the symbol of mass. There are no other dimensional parameters. Therefore, it is natural to find the self-similar solution of the problem, where self-similarity should pertain to the second type. Let us present the solution in the form of (12.3), (12.5)-(12.7). In accordance with plane symmetry we shall designate the coordinate of the shock wave, counted off from the surface of the star $x = 0$, through $X(t)$.

As the scale of density ρ_0 one should take the magnitude of density of undisturbed gas in front of the shock wave front. Inasmuch as the wave spreads through a gas of variable density, this scale depends on time, or on the coordinate of the front X, which is all the same (see end of § 2). Namely, the scale of ρ_0 is equal to

$$\rho_0 = \rho_{00}(X) = bX^{\delta}. \tag{12.29}$$

As also in the problem about the convergence of a shock wave to the center, we shall take the beginning of the reading of time $t = 0$ as the moment of emergence of the shock wave on the surface, in accordance with which we shall change the sign of t in the self-similar law:

$$X = At^{\alpha} \rightarrow X = A(-t)^{\alpha}.$$

Thus, we find the solution in the form

$$\left.\begin{aligned} &\rho=\rho_0 g(\xi), \quad p=\rho_0 \dot{X}^2 \pi(\xi), \quad u=\dot{X} v(\xi), \\ &\xi=\frac{x}{X}, \quad \rho_0=bX^{\delta}, \quad X=A(-t)^{\alpha}. \end{aligned}\right\} \qquad (12.30)$$

Equations (12.4) for representatives in this case take on the form ($\nu = 1$)

$$\left.\begin{aligned} \delta+(v-\xi)(\ln g)'+v'=0, \\ (\alpha-1)\alpha^{-1}v+(v-\xi)v'+\frac{\pi'}{g}=0, \\ (v-\xi)(\ln \pi g^{-\gamma})'+\lambda=0, \\ \lambda=2(\alpha-1)\alpha^{-1}-(\gamma-1)\delta. \end{aligned}\right\} \qquad (12.31)$$

Boundary conditions on the front of a shock wave, which is assumed to be strong, are expressed by formulas (2.16), whence follows the boundary condition for representatives, analogous to (2.17): when $\xi = 1$

$$g(1)=\frac{\gamma+1}{\gamma-1}, \quad v(1)=\frac{2}{\gamma+1}, \quad \pi(1)=\frac{2}{\gamma+1}. \qquad (12.32)$$

At the time of emergence of the shock wave on the surface, i.e., when $X = 0$, for any value of x, different from zero, self-similar coordinate $\xi = \infty$. Gas-dynamic magnitudes at any finite value of x at the time of emergence should be limited. This puts an additional boundary condition on the unknown functions when $\xi = \infty$.

The procedure of the solution is fully analogous to the solution of the problem about focusing of a shock wave. We introduce new representatives: V, G, Z, and obtain a system corresponding to (12.15). The sytem is reduced to one first order differential equation with respect to V and Z and two quadratures; actually, instead of the two quadratures we obtain one quadrature and one algebraic relationship between variables, i.e., the integral of adiabaticity. The eigenvalue of the system of equations, exponent α is found by the method of trial-and-error, by means of numerical integration of the equation for function Z(V), from the condition that the integral curve passes through the proper singular point. As also earlier, the singular point corresponds to the ξ_0-line on plane x, t, which is the C_--characteristic and limits the region of influence on the motion of the front of the shock wave.

In [8] the value of the index of self-similarity was found for the values of $\delta = 13/4 = 3.25$, $\gamma = 5/3$, equal to $\alpha = 0.590$.

In work [9] the exponents α were found for a number of other values of δ and γ. These results are given in Table 12.1.

Table 12.1

γ \ δ	3,25	2	1	0,5
5/3	0,590	0,696	0,816	0,877
7/5		0,718	0,831	0,906
6/5		0,752	0,855	0,920

The fact that the index of self-similarity α is always less than unity indicates that the shock wave is continuously accelerated:

$$X \sim |t|^{\alpha}, \quad |\dot{X}| \sim |t|^{-(1-\alpha)} \sim X^{-\frac{1-\alpha}{\alpha}}, \quad |\dot{X}| \to \infty \text{ when } X \to 0.$$

In accordance with this the temperature on the front increases without limit, which is proportional to the square of speed of the front of square of the speed of sound: $T \sim |\dot{X}|^2 \sim X^{\frac{-2(1-\alpha)}{\alpha}}$. Unlimited temperature increase, as mentioned above, is connected with the fact that a finite amount of energy is imparted without limit to the decreasing quantity of gas. Pressure on the front of the shock wave decreases with the approach of the front to the surface, in spite of the growth of speed, since the density before front decreases faster than the temperature increases (or square of speed):

$$p_1 \sim \rho_0 \dot{X}^2 \sim X^{\delta - \frac{2(1-\alpha)}{\alpha}}.$$

It is easy to check with the help of the data in Table 12.1 that the exponent of X in this formula is always positive, i.e.,

$$p_1 \to 0 \text{ when } X \to 0.$$

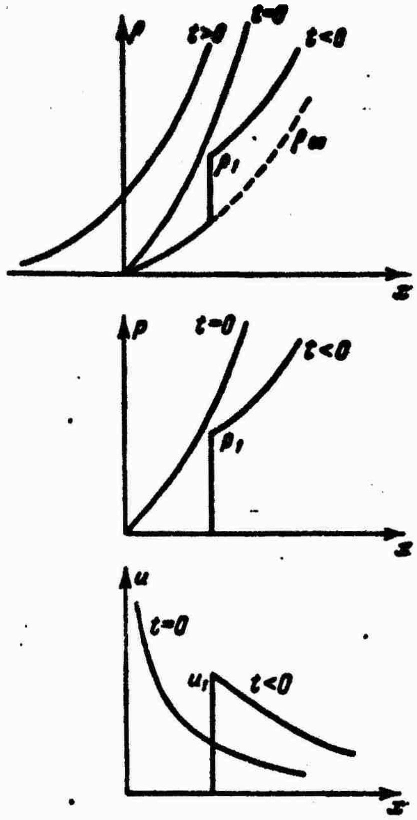

Fig. 12.6. Profiles of density, pressure, and speed upon emergence of a shock wave on the surface of a star. t < 0 — before emergence, t = 0 — moment of emergence, t > 0 — after emergence.

Limiting distributions of magnitudes with respect to coordinate x at the time of emergence of the shock wave on the surface t = 0, X = 0 (t = 0, x ≠ 0 correspond to $\xi = \infty$), obviously coincide in form with the laws on the front of the shock wave. This, as also in the problem about the shock wave convergent to the center, follows simply from considerations of dimension. We obtain at the time t = 0:

$$u \sim x^{-\frac{1-\alpha}{\alpha}};\quad T \sim u^2 \sim c^2 \sim x^{-\frac{2(1-\alpha)}{\alpha}};$$

$$\rho \sim x^{\delta};\quad p \sim x^{\delta-\frac{2(1-\alpha)}{\alpha}}.$$

(Certainly, the same laws follow from equations in the limit $\xi \to \infty$). Density in the final distribution is increased a determined number of times as compared to density in the initial state.

Distributions of magnitudes with respect to coordinate x before emergence and at the moment of emergence of the wave on the surface are schematically shown in Fig. 12.6.

Energy of gas, when t = 0, enclosed in a layer from x = 0 to x in a column with a cross section of 1 cm^2, is proportional to the magnitude

$$\int_0^x \rho u^2 dx \sim \int_0^x p\,dx \sim x^{\delta+1-\frac{2(1-\alpha)}{\alpha}}.$$

When x → ∞ the energy tends to infinity; there is no integral of energy. Energy of a layer of finite thickness is finite and when x → 0 it tends to zero. In distinction from the convergent shock wave on the edge, when $x \to 0$, the density of energy proportional to pressure also tends to zero. Only temperature increases without limit, i.e., energy of a unit of mass.

"Infinite" energy is imparted to the vanishing small mass of gas. Certainly, in reality, temperature cannot grow ad infinitum, as this is obtained in the mathematical solution. Thus, for instance, when a shock wave approaches so close to the surface that the remaining small mass of the layer from $x = 0$ to $x = X$ contains a small number of gas-kinetic paths, in general, the gas-dynamic consideration is meaningless. Infinite temperature rise can be limited by causes of physical character: losses of energy in the radiation of a highly heated substance.

As also in the problem about convergence of a shock wave to the center, a self-similar solution is valid only in a limited region with dimensions of the order of the coordinate of the front X. Far from the front, when $x \gg X$, the solution is not self-similar and depends on the conditions of appearance of the shock wave. The nonself-similar solution changes into a self-similar one when $x \sim X$.

After emergence of the shock wave on the surface the gas passes into a vacuum, and the initial distributions of density, pressure, and speed are given by root laws when $t = 0$. As shown in [9], the solution in the stage of expiration is also self-similar, but, of course, has quite another character (flow is continuous, without shock waves). Approximate distribution of density in some moment $t > 0$ is shown in Fig. 12.6.

§ 12. Concerning the Problem of Outbursts of Supernovae and the Origin of Cosmic Rays

The thought has been stated that the origin of cosmic rays, i.e., the protons and nuclei with colossal energy which are present in the universe and fall to the earth, is connected with outbursts of supernovae. Such a theory was developed by V. L. Ginzburg and I. S. Shklovskiy (see survey [10]). The process of "unlimited" growth of amplitude of a shock wave and cumulation of energy during emergence of a shock wave from a depth to the surface of a star could also be a cause of acceleration of particles to colossal energies. This idea was used by Colgate and Johnson; they investigated similar process in detail [11] and showed on the basis of calculations that a certain quantity of substance, ejected from the surface during an outburst of supernova, obtains ultrarelativistic speeds and kinetic energies, corresponding to the energies of cosmic rays. (The greatest energies of particles, which are presently observed in the spectrum of cosmic rays, have the order of 10^8 Bev = 10^{17} ev; 1 Bev = 10^9 ev). Below we shall present the results of the work of Colgate and Johnson. In the center of supernovae the temperatures reaches ~300-500 kilo-electron-volts ($\sim 5 \cdot 10^9$ °K). With such temperature, nuclear fusion proceeds up to the formation of the stablest element, i.e., iron. The more external layers consist of lighter elements: carbon, nitrogen, oxygen; even nearer to the surface is helium; finally, the most external layers consist of hydrogen. Astronomical data indicate that during an outburst a supernova ejects a mass of substance of the order of one tenth of all the mass of the star and of the order of the mass of the sun, equal to $M_\odot = 2 \cdot 10^{33}$ g.

Calculations of mechanical and radiation equilibriums of a star with a mass equal to 10 $M_\odot$, give a picture of distribution of density and temperature along the radius, shown in Fig. 12.7 .* In the center

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*In conditions of radiation equilibrium, density depends on temperature according to the law $\rho \sim T^{13/4} = T^{3.25}$. Namely, proceeding from of the star the density is higher than 10^8 g/cm^3, and on the surface it drops to zero. In any case, propagation of an ordinary shock wave is traced to layers with a density of $\rho \sim 10^{-5}$ g/cm^3.

It is considered that the power source of a shock wave is the so-called gravitational instability which takes place in the adiabatic equation of state with adiabatic exponent $\gamma < 4/3$. In the central regions of a star, at a temperature of 500 kilo-electron-volts, the nuclei strongly dissociate; in the process of dissociation, as it is known, the heat capacity of the substance is sharply increased and the adiabatic exponent decreases. As a result of gravitational instability the perturbations, which appear once for any reason, are amplified. The appearing impulse of pressure spreads, and this leads to the formation of a shock wave, which heads from the central regions to the surface. The substance behind the shock wave scatters from the center, and the external layers, due to amplification of the wave, obtain very high speeds.

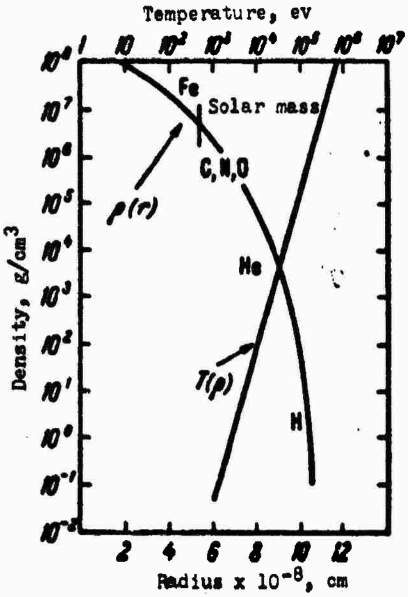

Fig. 12.7. Distributions of density and temperature before the outburst of a star. $\rho \sim T^{3.25}$ in accordance with the conditions of radiation equilibrium.

Possessing great kinetic energy of scattering, the substance in the peripheral layers surmounts the gravity force and after emergence of the shock wave to the surface it is detached from the star: the star

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[FOOTNOTE CONT'D FROM PRECEDING PAGE].
this there was selected in [8] a law of distribution of density at the surface $\rho \sim x^{3.25}$, since in a certain layer near the surface the temperature weakly depends on coordinate x (on the surface of a star the temperature is not equal to zero). Figure 12.7 notes the radius of the external layer, whose mass is equal to the mass of the sun. This layer, we must assume, is also ejected during the outburst. The zones, which contain those or other elements are noted approximately.

as if casts the shell from itself. This phenomenon is well-known in astrophysics. They consider that the Crab nebula was formed in this manner. An evaluation indicates that for surmounting the forces of gravitation during ejection of a mass equal to the mass of the sun, there is necessary an energy of the order of 10^{52} erg. Such, consequently, is the energy that is liberated in the center of a star and goes for the formation of a shock wave.

Hydrodynamic calculation of propagation of a shock wave from such a source gives the values of speed behind the front of a shock wave that are shown on curve I in Fig. 12.8. Along the axis of abscissas on this figure there is plotted the initial density of the substance before the front. Curve II shows what speed the layer obtains with given density after emergence of the wave to the surface and expansion of the substance. Speed after expansion increases approximately twice as compared to the speed at the time of passage of the front of the shock wave.

From Fig. 12.8. it is clear that the peripheral layers, where the density is approximately less than 30 g/cm^3, obtain speeds in the amplified shock wave higher than 10^{10} cm/sec , which is 1/3 of the velocity of light c. Therefore the calculation of motion of a shock wave through these peripheral layers requires calculation of relativistic effects.

In work [11] there was made a numerical calculation of motion within the confines of relativistic gas dynamics, and there also was found an approximate analytic solution to the problem, founded on the use of equations in characteristics and relativistic analogs of Riemann invariants. It is interesting to note that internal energy behind the front of such a powerful shock wave is almost wholly

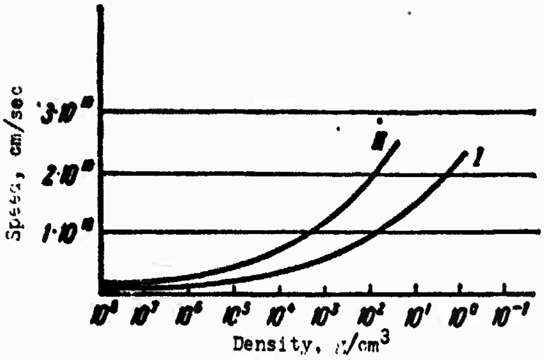

Fig. 12.8. Speed of a substance depending upon its density in the initial moment before arrival of a shock wave. Curve I — speed directly behind the front of the wave, curve II — speed after expansion.

concentrated in equilibrium thermal radiation. Approximate solution shows that the final kinetic energy per gram, which is obtained by a substance located in a layer with initial density ρ_0 g/cm^3, in order of magnitude is equal to $c^2\left(\frac{30}{\rho_0}\right)^{0.64}$ erg/g. If we consider that in hydrogen 1 erg/g corresponds to approximately 10^{-12} ev/proton = = 10^{-21} Bev/proton, then we obtain that the kinetic energy of the order of 10^4 Bev is picked up by the particles that were earlier located in the layer with initial density $\rho_0 \sim 10^{-5}$ g/cm^3. Mass of the layer of a star, external with respect to a spherical surface with such initial density, composes approximately 1 g/cm^2 from the calculation per unit of surface. So the thin layer is no longer in a state to hold or "lock" the thermal radiation, which in the more external layers is unbalanced. Therefore, propagation of a shock wave through the more external layers no longer can occur as in equilibrium conditions.

Further propagation of the shock wave through a gas of lower density, as the authors of [11] note, in an essential form is connected with the mechanism of plasma oscillations. The shock wave reaches such a surface, where the Debye length becomes comparable with the scale of length of the remaining external layer. Calculations show that this occurs on a radius where the initial density is $\rho_0 \sim 10^{-12}$ g/cm^3. Particles in a shock wave at such a radius are accelerated to energies of $\sim 10^8$ Bev, coinciding with the highest observed energies of cosmic rays.

It is important to check if the quantity of particles accelerated during outburst of supernovae is retained up to energies of cosmic rays in order to ensure an available "reserve" of cosmic rays in the Galaxy. Initial density of the substance, which after passage of the shock wave is accelerated to an energy of ~10 Bev, is equal to approximately 1 g/cm^3. Mass of a star in a layer that is external with respect to the spherical surface, where $\rho_0 \sim 1$ g/cm^3 composes ~10^{26} g or $6\cdot10^{49}$ protons. It is possible to say that during an outburst $6\cdot10^{49}$ protons will obtain an energy exceeding 10 Bev. The "life" of an energy proton in the galaxy with average density of matter in the galaxy ~0.1 particle/cm^3 composes $\tau \sim 5\cdot10^8$ years.

This means that in ~$5\cdot10^8$ years after the "beginning" of outbursts in the galaxy there will be established a stationary number of protons N. Outbursts of supernovae occur approximately once every 100 years. Consequently, every year $6\cdot10^{49}/100 = 6\cdot10^{47}$ protons are born, and N/τ protons "die" each year. From the condition of stationarity, $N/\tau = 6\cdot10^{47}$ protons/year, follows $N = 3\cdot10^{56}$. The volume of the Galaxy is $V \sim 5\cdot10^{68}$ cm^3. Average density of energy protons is $N/V \sim$ $\sim 6\cdot10^{-13}$ cm^{-3}, and flow is on the order of $Nc/V \sim 2\cdot10^{-2}$ cm$^{-2}\cdot$sec^{-1}. This magnitude agrees with observations. For the creation of cosmic rays in the galaxy according to the presented theory, ~$5\cdot10^6$ outbursts of Supernovae were demanded.

4. Motion of a Gas Under the Action of a Brief Shock

§ 13. Formulation of Problem and General Character of Motion

Let us imagine a half-space $x > 0$, occupied by an ideal gas with constant heat capacity. In initial moment $t = 0$ the density of the

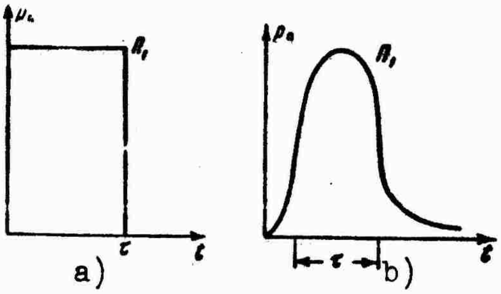

Fig. 12.9. Forms of initial pressure.

gas is identical everywhere and is equal to ρ_0, while pressure, temperature, and initial speed of sound are equal to zero. Half-space $x < 0$ is empty; surface $x = 0$ constitutes the boundary between the gas and vacuum.

Let us assume that the external surface of the gas experiences a brief pulse of pressure (surface of gas is subjected to a shock). Various specific methods of realizing a brief shock are possible.

1) During a shorttime τ into the gas there is inserted a flat piston with constant speed U_1, which creates in the gas a pressure P_1. With an accuracy of numerical coefficient of the order of unity (depending on adiabatic exponent γ) $P_1 \approx \rho_0 U_1^2$. The speed of the shock wave D is close to U_1; it is created under the action of the piston. Upon the expiration of time τ the piston is "instantly" retracted, and the gas, experiencing a brief shock, turns out to be left to itself (the pressure pulse is shown in Fig. 12.9a).

2) On the surface of the gas a thin layer of explosive is detonated. If the mass thickness of the layer is equal to m g/cm^2, and caloricity, i.e., energy release per gram, is equal to Q erg/g, in the explosion there is released an energy of $E = mQ$ erg/cm^2. The products of the explosion scatter with a speed of $U_1 \approx \sqrt{Q}$. Inasmuch as the products scatter in both directions and everything was stationary up to the moment of the explosion, the total pulse is equal to zero; however the pulse of the products moving in one direction, in order of magnitude is equal to $I \approx mU_1 \approx m\sqrt{Q}$ (per cm^2 of surface).

In the gas the products of explosion create a shock wave with pressure of the order $P_1 \approx \rho_0 U_1^2$. Time of action of pressure τ is determined from the condition that during the time τ the energy and pulse are transmitted from the products of the explosion to the gas:

$$\tau \sim \frac{E}{\Pi_1 U_1} \sim \frac{I}{\Pi_1} \sim \frac{m}{\rho_0 \sqrt{Q}} \sqrt{Q\tau}.$$

During that time the shock wave in the gas will pass a distance of $\sim U_1 \tau \sim \sqrt{Q\tau}$ and will envelope a mass of $\sim \rho_0 \sqrt{Q\tau} \sim m$, i. e., on the order of the mass of the explosive.

3) On the surface of the gas, with speed U_1, a thin plate runs with a small mass m g/cm^2. Under the action of the shock of the plate in the gas there will form a shock wave which spreads with speed $D \approx \approx U_1$. Pressure in the gas is then $P_1 \approx \rho_0 U_1^2$. Initial momentum and energy of the plate, $I = mU_1$, $E = \frac{mU_1^2}{2}$, are transmitted to the gas during the time of deceleration of the plate τ, which is on the order of $\tau \approx \frac{E}{P_1 U_1} \approx \frac{I}{P_1} \approx \frac{m}{\rho_0 U_1}$. During that time the shock wave in the gas passes a distance of $U_1 \tau$ and envelopes a mass of $\rho_0 U_1 \tau \approx m$.

Thus, in general we shall consider that on the surface of the gas there acts a pressure that drops rather quickly in time, as shown in Fig. 12.9b. The pressure curve can be presented in the form of $p_p = P_1 f(t/\tau)$, where f is the function characterizing the form of the pressure pulse. Subsequently, for concreteness and convenience of the statements where the initial conditions will be discussed, we will operate on the "piston" concept, as in the first example. We shall then consider that all conclusions with equal success can also be transferred to any other methods of realizing a shock.

The problem consists in finding the laws of motion of the gas, i.e., the functions $p(x, t)$, $\rho(x, t)$, $u(x, t)$, upon the expiration of a time sufficiently large as compared to the time of the shock τ, i.e., we must find the asymptotic conditions when $t/\tau \gg 1$ for a given curve of action of external pressure. It can also be formulated somewhat differently. Preserving the form of the curve $f(t/\tau)$, we shall direct time τ to zero, and pressure P_1, to infinity, and shall find the thus obtained limiting solution of equations of gas dynamics for finite times. The solution of problem should in particular answer the question of according to what law should pressure P_1 increase when $\tau \rightarrow 0$ in order to ensure the given finite pressure in the gas in the finite time t. For instance, if the solution contains the combination $P_1\tau^{\beta}$, this means that when $\tau \rightarrow 0$, P_1 should grow as $\tau^{-\beta}$.

The presented problem was set up and investigated in the work of one of the authors of [12], where he clarified the physical peculiarities of the appearing motion and the mathematical solution. Investigation of equations and numerical integration was conducted by V. B. Adamskiy [13]. A. I. Zhukov and Ya. M. Kazhdan [14], Häfele [15], and Hoerner [16] found an analytic solution for one particular case ($\gamma = 7/5$). The last two works are the development of an article by Weizsäcker [17], who posed the question about the limits of change of the index of self-similarity during plane motions. It is necessary to note that in [15, 16, 17] the physical meaning of the solution obtained by formal means was not clarified.

The general character of the motion appearing under the action of a brief shock is illustrated Fig. 12.10. Through an undisturbed gas there spreads a shock wave, on the front of which there is attained limiting compression $h = \frac{\gamma + 1}{\gamma - 1}$. From another direction the gas is freely expanded into a vacuum; on the boundary with the vacuum the density and pressure drop to zero. Behind the front of the shock wave the pressure, density, and speed decrease, whereby in a certain point the speed changes sign, since directly behind the front the gas moves to the right, and at the boundary it scatters into the vacuum to the left. Amplitude of the shock wave decreases in time.

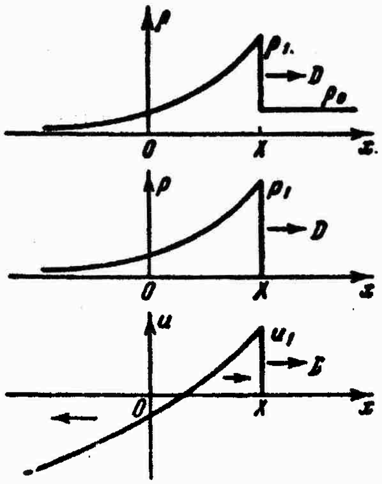

Fig. 12.10. Profiles of density, pressure, and speed in the problem concerning a brief shock.

Solution of the problem about instantaneous pressure pulse should give the answer to the question about maximum possible speed of decrease of amplitude of a plane shock wave during propagation through a gas with constant initial density. It is clear that if the action of pressure is extended in time, this only supports the shock wave and delays its damping.

The character of the limiting solution does not depend on the specific form of pressure pulse, i.e., on the form of function $f(t/\tau)$, if it only drops rather quickly. It was noted above that under the action of pressure P_1 during a shock the gas obtains the speed $U_1 \sim \sqrt{\frac{P_1}{\rho_0}}$. With the same speed in order of magnitude the boundary of the gas scatters into the vacuum. When we pass to the limit $\tau \to 0$, $P_1 \to \infty$, the speed of the boundary tends to infinity, so that distributions of p, ρ, and u in the limiting solution shown in Fig. 12.10 spread to the left to $x = -\infty$.

§ 14. Self-Similar Solution and Laws of Conservation of Energy and Momentum

The motion which appears directly after the application of pressure momentum is of course not self-similar. It is characterized by scales of time τ and length $x_0 = \sqrt{P_1/\rho_0}\,\tau$ and depends on the form of the curve of applied pressure $f(t/\tau)$. However, upon the expiration of a sufficiently long time, in moments $t \gg \tau$, when the front of the shock wave departs to a distance of $X \gg x_0$, the initial scales of τ and x_0, very small as compared to the natural scales of motion t and X, no longer will characterize the process. Limiting motion, corresponding to the stages $t \gg \tau$, $X \gg x_0$, or, the same, corresponding to passage to the limit $\tau \to 0$, will be self-similar. The singular scale of length in this motion is the actual variable coordinate of the front of the shock wave X, and the scale of speed is the speed of the front $\dot{X}$. Solution of the equations consequently, should be found in self-similar form:

$$\varrho = \varrho_0 g(\xi); \quad u = \dot{X} v(\xi); \quad p = \varrho_0 \dot{X}^2 \pi(\xi); \quad \xi = \frac{x}{X} = \frac{x}{At^{\alpha}}. \qquad (12.33)$$

Before we concern ourselves with the mathematical solution of the equations, we should solve the question of which of the two types does the self-similar motion belong to, and is it impossible to determine the index of self-similarity α from considerations of dimension or laws of conservation. In distinction from the two problems considered above: about the convergence of a shock wave to the center and about emergence of a shock wave to the surface of a star, in the considered problem in every moment of time t the motion involves a fully determined finite mass of gas $\rho_0 X$ (per cm^2 of surface).

Inasmuch as after cessation of the action of the piston, which accomplished the shock through the surface of the gas, the gas is not affected very much by external forces (pressure on boundary with vacuum is equal to zero) and in the gas momentum and energy must be retained. Momentum of gas is equal to the momentum of pressure of the piston:

$$I = \int_0^\infty p_{\text{п}}\, dt = \Pi_1 \tau \int_0^\infty f\left(\frac{t}{\tau}\right) d\left(\frac{t}{\tau}\right).$$

With an accuracy of numerical coefficient this magnitude is equal to $P_1\tau$.

Energy of the gas is equal to the work performed by the piston during the time of action of pressure. To exactly calculate this work would demand the solution of equations of gas dynamics in the stage of action of the piston, since the work is equal to $\int_0^\infty p_p u_p dt$, where $u_p(t)$ is the speed of the piston, which beforehand was unknown (only pressure curve $p_p(t)$ was assigned).

However, with an accuracy of numerical coefficient, depending on the form of function $f(t/\tau)$, this work is equal to

$$E \approx \Pi_1 U_1 \tau \approx \Pi_1 \sqrt{\frac{\Pi_1}{\rho_0}}\,\tau = \Pi_1^{\frac{3}{2}} \tau \rho_0^{-\frac{1}{2}}$$

(U_1 is the scale of speed of the piston).

If we place pressure, speed, and density in integral expressions for momentum and energy of the entire gas in self-similar form (12.33) and consider that the integrals in the cold, undisturbed region $X < x < \infty$ disappear, the laws of conservation of momentum and energy (per cm^2 of surface) can be written in the form

$$I = \int_{-\infty}^{\infty} \rho u \, dx = \rho_0 \dot{X} X \int_{-\infty}^{1} g v \, d\xi = \text{const}, \tag{12.34}$$

$$E = \int_{-\infty}^{\infty} \left(\rho \frac{u^2}{2} + \frac{1}{\gamma - 1} p\right) dx = \rho_0 \dot{X}^2 X \int_{-\infty}^{1} \left(\frac{g v^2}{2} + \frac{1}{\gamma - 1} \pi\right) d\xi = \text{const}. \tag{12.35}$$

It would be natural to consider the dimensionless integrals to be constant. Then each of the two conditions taken separately would give the possibility to determine the index of self-similarity α. Ther condition of conservation of momentum would give $\dot{X}X$ = const, whence $X \sim t^{1/2}$, $\alpha = 1/2$. From the condition of conservation of energy follows $\dot{X}^2 X$ = const, where upon $X \sim t^{2/3}$ and $\alpha = 2/3$.

But taken together, these conditions contradict each other, since they lead to different indices of α. There appears a paradoxical situation in which the laws of conservation of momentum and energies, which are the bases of the equations of gas dynamics, cannot be simultaneously carried out. This creates the impression that the problem does not have a self-similar solution, the substitution of which in conditions of conservation led to a contradiction.

The solution of this contradiction, however, consists in another solution. The fact is that the self-similar solution, which exists and which will be found below, in reality belongs to the second type. The index of self-similarity α is not found from laws of conservation or considerations of dimension, but by means of the solution of equation for representative functions, from the condition of passage of the true solution through a singular point, just as in the problems considered in the preceding sections.

In order to immediately solve the described paradox, let us note that at the value of adiabatic exponent $\gamma = 7/5$, the index of self-similarity, as the solution shows, is equal to $\alpha = 3/5$.* It is included between the values of α, dictated by the conditions of conservation of momentum and energy $1/2 < 3/5 < 2/3$. It will be shown below that at any value of adiabatic exponent, $1 < \gamma < \infty$, the index of self-similarity α is included in the shown limits: $1/2 < \alpha < 2/3$.

The index of self-similarity $\alpha = 3/5$ corresponds to the dimension of parameter A in the law $X = At^{\alpha}$, equal to $[A] = \text{cm} \cdot \text{sec}^{-3/5}$. We already know (see § 5) that limiting self-similar motion does not

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*In general, at an arbitrary value of γ index α is not expressed in the form of a fraction with integral numerator and denominator. However, fortunately, when $\gamma = 7/5$ the solution of self-similar equations can be found in analytic form, and α is then equal to $3/5$ (see below).

completely "forget" about the initial conditions, but from the extensive information included in the initial condition it "selects" and "remembers" one specific constant A, which somehow characterizes the initial "shock." In this case, from the information given by the pressure curve on the piston, $p_p = P_1 \times f(t/\tau)$ (and magnitude of initial density ρ_0), the limiting solution "selects" one parameter A, equal, in order of magnitude of the following combination from characteristic scales, to:

$$A \approx \left(\frac{\Pi_1}{\rho_0}\right)^{\frac{1}{2}}\tau^{1-\alpha} = \left(\frac{\Pi_1}{\rho_0}\right)^{\frac{1}{2}}\tau^{\frac{2}{5}}\text{см}\cdot\text{сек}^{-\frac{3}{5}}. \qquad (12.36)$$

The numerical coefficient in the law of proportionality is determined by the form of the pressure curve $f(t/\tau)$.

Hence, one may see according to what law should pressure on piston P_1 tend to infinity, if we direct τ to zero so that in the limiting motion we obtain finite (not equal to 0 or ∞) pressure at finite distance. For the existence of a limiting solution it is necessary that parameter A has a finite value, i.e., it is necessary that the product of $P_1^{1/2}\tau^{1-\alpha}$, equal to $P_1^{1/2}\tau^{2/5}$ in the case of $\gamma = 7/5$, remains finite when $\tau \to 0$. Consequently, when $\tau \to 0$, P_1 should grow as $P_1 \sim \tau^{-2(1-\alpha)} \sim \tau^{-4/5}$.

Now it is possible to clarify the question about the fulfillment of the laws of conservation. The momentum which the piston imparts to the gas, or the shock momentum, in order of magnitude are equal to $I \sim P_1\tau$, i.e., are proportional to $I \sim P_1\tau \sim \tau^{2\alpha-1} \sim \tau^{1/5}$. When $\tau \to 0$, momentum $I \to 0$. Consequently, full momentum in limiting, self-similar motion is equal to zero (momentum of the gas moving with the shock wave to the right is accurately compensated by the momentum of the gas scattering into the vacuum to the left; see Fig. 12.10). The law of conservation of momentum is written in form

$$I=\rho_0\dot{X}X\int\limits_{-\infty}^{1}gv\,d\xi\sim t^{\frac{1}{5}}\int\limits_{-\infty}^{1}gv\,d\xi=0.$$

If follows from this only the fact that the representative functions have to satisfy the condition $\int\limits_{-\infty}^{1} gv\, d\xi = 0$. As can be seen, it is impossible to consider the magnitude $\dot{X}X$ as constant and thus to determine the index of self-similarity α.

The energy which the piston imparts to the gas in order of magnitude is equal to $E \sim P_1^{3/2}\tau\rho_0^{-1/2}$. It is proportional to $E \sim P_1^{3/2}\tau \sim \sim \tau^{3\alpha-2} \sim \tau^{-1/5}$. When $\tau \to 0$, $E \to \infty$. Total energy of gas in self-similar motion turns out to be infinite. Law of conservation of energy

$$E=\rho_0\dot{X}^2X\int\limits_{-\infty}^{1}\left(\frac{gv^2}{2}+\frac{1}{\gamma-1}\pi\right)d\xi\sim t^{-\frac{1}{5}}\int\limits_{-\infty}^{1}\left(\frac{gv^2}{2}+\frac{1}{\gamma-1}\pi\right)d\xi=\infty$$

only indicates the divergence of the integral from dimensionless functions, but says nothing about magnitude $\dot{X}^2X$ (from the law of conservation of energy it is also impossible to determine the index of self-similarity). Infinity of energy and divergence of integral of energy are connected with the fact that in exact self-similar motion, which corresponds to limit $\tau \to 0$, the speed of scattering of the gas boundary into the vacuum is infinite (see end of § 13). The kinetic energy is also infinite on the boundary, since the square of "speed" v^2, when $\xi \to -\infty$, tends to infinity faster than density g decreases.

The physical meaning of the infinity of energy in self-similar motion will be explained below. Let us note here only that the energy of gas, of course, is limited and is equal to the work accomplished by the piston. Simply, a self-similar solution inapplicable to a small mass at the gas boundary, which introduces a divergence into the integral of energy.

§ 15. Solution of Equations

The general method of finding a self-similar solution to the problem of a brief shock in principle does not differ from the method solving problems about a convergent shock wave or about propagation of a shock wave through a gas whose density decreases with distance. by root law (see §§ 2 and 3 of this chapter). As also earlier, we shall find the solution of equations of gas dynamics (12.1) in self-similar form (12.33) and obtain a system of ordinary differential equations for representatives π, v, and g.

These equations coincide with equations (12.31) if we put the number of δ in them equal to zero (in accordance with constancy of the density scale):

$$\left.\begin{aligned} (v-\xi)(\ln g)'+v'=0, \\ (\alpha-1)\alpha^{-1}v+(v-\xi)v'+g^{-1}\pi'=0, \\ (v-\xi)(\ln \pi g^{-\gamma})'+2(\alpha-1)\alpha^{-1}=0. \end{aligned}\right\} \qquad (12.37)$$

Boundary conditions on the front of the shock wave when $\xi = 1$ were written out in § 11 (formulas (12.32)). On the boundary of the gas with the vacuum the pressure and density return to zero, and speed to $(-\infty)$, i.e., when $\xi = -\infty$, $\pi(-\infty) = 0$, $g(-\infty) = 0$, $v(-\infty) = -\infty$.

After a series of transformations the equations are reduced, as usual, to one first order differential equation, one quadrature, and one algebraic relationship between all variables, i.e., the integral of adiabaticity. The index of self-similarity is determined from the condition that the sought solution of the differential equation passes through a singular point.

Actually, in [13, 14] the equations were written and were solved not in Euler, but in Lagrange coordinates. In a one-dimensional plane case at constant initial density the Lagrange form of notation leads to simpler and more convenient relationships. It is clear that no principally new transition from Euler coordinates to Lagrange is introduced. The Lagrange coordinate is defined as the mass of gas (per cm^2 of surface) which is counted off from the boundary with the vacuum

$$m=\int_{-\infty}^{x}\rho\,dx,\quad dm=\rho\,dx. \tag{12.38}$$

Instead of time, into the scale functions it is convenient to introduce the Lagrange coordinate of the front of the shock wave $M = \rho_0 X$, i.e., the mass of the gas (per cm^2 of surface), which is enveloped by motion to moment t. The self-similar variable is the ratio

$$\eta=\frac{m}{M}, \tag{12.39}$$

which varies from $\eta = 0$ (on the boundary of the gas with vacuum) to $\eta = 1$ (on the front of the shock wave).

Thus, the solution is written in the form

$$p=B\rho_0M^{-n}f(\eta),\qquad u=\sqrt{B}\,M^{-\frac{n}{2}}w(\eta),\qquad \rho=\rho_0q(\eta), \tag{12.40}$$

where B is the parameter of the problem connected with parameter A in law $X = At^{\alpha}$ and replacing it in the new notation. f, w, and q are the new representatives. The new index of self-similarity n is simply connected with the old one, α. Actually,

$$M=\rho_0X\sim t^{\alpha},\quad u\sim M^{-\frac{n}{2}}\sim t^{-\frac{\alpha n}{2}},\quad u\sim\dot{X}\sim t^{\alpha-1}.$$

Hence $-\alpha n/2 = \alpha - 1$ and

$$n=\frac{2(1-\alpha)}{\alpha},\quad \alpha=\frac{1}{1+\frac{n}{2}}. \tag{12.41}$$

From the mathematical side of the question, the sequence of transformations of the equations, their investigation, and specific methods of solution can be seen in articles [13, 14]. Let us stop here more specifically on the results for the particular case of $\gamma = 7/5$, for which it is possible to find an exact analytic solution of the equations.

In examining the analytic solution all the basic features of the process become especially clear.

Indices α and n when $\gamma = 7/5$ are equal to: $\alpha = 3/5$; $n = 4/3$. The solution in Lagrange coordinate has the form

$$f=\eta, \quad w=-\frac{1}{2}\sqrt{\frac{5}{6}}\left(\eta^{-\frac{2}{3}}-3\right), \quad q=6\eta^{\frac{5}{3}}. \tag{12.42}$$

Distributions of pressure, density, and speed with respect to mass are shown in Fig. 12.11. Let us note that by definition $f = p/p_1$, $w\sqrt{6/5} = u/u_1$, and $q/6 = \rho/\rho_1$, where subscript "1" denotes the magnitude on the front of the shock wave. With the help of determinations of the Lagrange coordinate (12.38) and self-similar variable η (12.39) it is easy in solution (12.42) to transfer to Euler variable $\xi = x/X$. Actually, at the given moment t, i.e., when M = const:

$$dm=\varrho\,dx; \quad \frac{dm}{M}=\frac{\varrho}{\varrho_0}\frac{dx}{X}, \text{whence } d\eta=q\,d\xi.$$

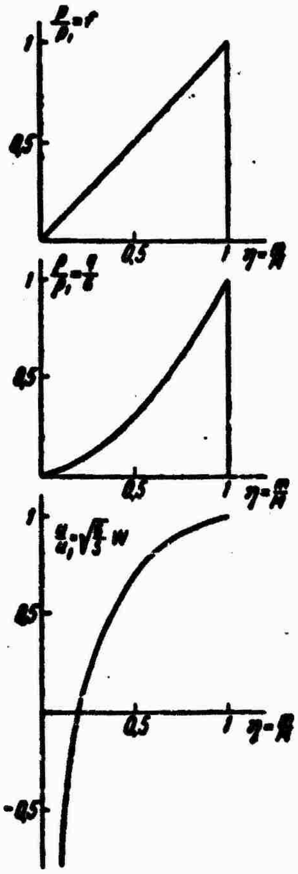

Fig. 12.11. Profiles of pressure, density, and speed in the problem of brief shock (in Lagrange coordinates), $\gamma = 7/5$.

Putting function $q(\eta)$ in this equation by the formula (12.42) and integrating with boundary condition $\eta = 1$ when $\xi = 1$ (on the front of the shock wave), we obtain

$$\eta=(5-4\xi)^{-\frac{3}{2}}, \quad \xi=\frac{1}{4}\left(5-\eta^{-\frac{2}{3}}\right). \tag{12.43}$$

Depending upon the Euler variable, functions f, w, and q have the form

$$f=(5-4\xi)^{-\frac{3}{2}}, \quad w=-\sqrt{\frac{5}{6}}(1-2\xi),$$
$$q=6(5-4\xi)^{-\frac{5}{2}}. \tag{12.44}$$

Representatives f, w, and q are connected with representatives π, v, and g, which we dealt with earlier, by the relationships:

$$\pi = \frac{5}{6} f, \quad v = \sqrt{\frac{5}{6}} w, \quad g = q^{*}). \qquad (12.45)$$

Distribution of pressure, density, and speed according to the Euler coordinate are shown in Fig. 12.12. It is interesting that pressure in linear form is distributed through mass, and speed, in space. Speed returns to zero and changes direction at point $\xi = 1/2$. The mass, included between the initial position of the gas boundary $x = 0$ and front of the wave, in every moment of time composes 90% of the whole mass set into motion. 10% of the mass, as a result of shock compression and subsequent expansion, is ejected to the left of the gas boundary. 78% of the mass moves to the right, and 22%, to the left.

Asymptotic behavior of the solution in the region of small density, when $\xi \to -\infty$ and $\eta \to 0$, is given by the expressions:

$$f \sim (-\xi)^{-\frac{3}{2}}, \quad w \sim \xi, \quad q \sim (-\xi)^{-\frac{5}{2}}, \qquad f = \eta, \quad w \sim \eta^{-\frac{2}{3}}, \quad q \sim \eta^{\frac{5}{3}}. \qquad (12.46)$$

The singular point through which there passes the solution of the differential equation of the problem corresponds to the values of self-similar variables $\eta_0 = 7^{-3/2} = 0.054$ and $\xi_0 = -1/2$.

As also in the problem of convergence of a shock wave, the ξ_0-line on plane x, t (η_0-line on plane m, t or m, M) is the characteristic ($dx/dt = u + c$; $dm/dt = \rho c$) which separates the region of influence. In Figs. 12.13 and 12.14, depicting diagrams of x, t and m, M, we have plotted the line of the front of the shock wave $\xi = 1$ and $\eta = 1$,

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*We shall let the reader, by means of direct substitution of functions π, v, and g by formulas (12.45) and (12.44) in equations (12.37) with $\gamma = 7/5$ and $\alpha = 3/5$, check that they indeed satisfy the equations (and boundary conditions of (12.32)).

special line $\xi = \xi_0$ and $\eta = \eta_0$, and the characteristic curve of both sets.* The special line is the C_+-characteristic. All characteristics of the C_+-set emerge from the origin of coordinates, whereby those which go to the right of the special line overtake the front of the shock wave, and those which go to the left, never overtake it. Thus, the state of motion in a relatively small mass, included between a boundary with a vacuum and a special line, does not affect propagation of the front of a shock wave.**

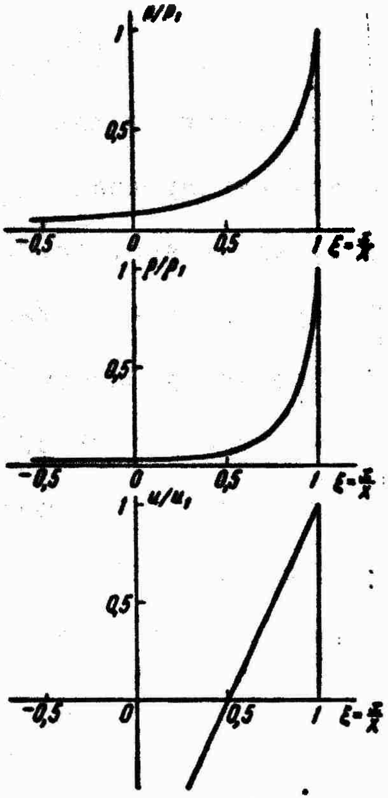

Fig. 12.12. Profiles of pressure, density, and speed in the brief shock problem (in Euler coordinates), $\gamma = 7/5$.

In [15, 16] by means of numerical integration of the equation they found the values of the exponents of self-similarity and for certain other adiabatic exponents γ. The results are given in Table 12.2.

Profiles of pressure, density, and speed at different values of the adiabatic exponent in a qualitative aspect are similar to profiles in the case of $\gamma = 7/5$ (see Figs. 2.11 and 2.12).

From the table it is clear that the shock wave attenuates slower,

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*Let us note that axis M is the $\eta = 0$-line, and axis t on plane x, t is the $\xi = 0$-line. Negative semi-axis x on plane x, t is the $\xi = -\infty$-line.

**In particular, the gas can border not with the vacuum, but with the "piston," the pressure on which drops according to sufficiently fast root law. Distortion of the state of motion in the region between the boundary and the ξ_0-line, connected with the presence of the piston, does not affect motion to the right of the ξ_0-line and the law of propagation of the shock wave, only if the pressure on the piston drops sufficiently fast. This is shown in the work of V. B. Adamskiy and N. A. Popov [18]. In this work, and also in the work of N. L. Krasheninnikova [19], a self-similar problem was considered concerning the motion of a gas under the action of pressure on a piston that is variable according to root law.

the larger the adiabatic exponent. However, attenuation is always faster than in case when the gas on the boundary does not scatter into a vacuum, but is motionless, as in the problem about the violent plane explosion.

Table 12.2

γ	1,1	7/5	5/3	2,8
n	1,515	4/3	1,275	1,045
α	0,57	3/5	0,612	0,656

If in plane x = 0 there occurs an instantaneous energy release E erg/cm^2, and the gas in plane x = 0 is always motionless or occupies the space on both sides of the plane, or is limited by a rigid wall), the energy is conserved and the shock wave attenuates according to the law

$$p_1 \sim X^{-1} \sim t^{-\frac{2}{3}}; \quad n = 1, \quad \alpha = \frac{2}{3}.$$

In the following paragraph it will be shown how the limitation n > 1 and $\alpha < 2/3$ follows from the law of conservation of energy at an arbitrary value of γ. In the same place we shall see that the law of conservation of momentum puts an opposite limitation on the exponents: $n < 2$, and $\alpha > 1/2$.

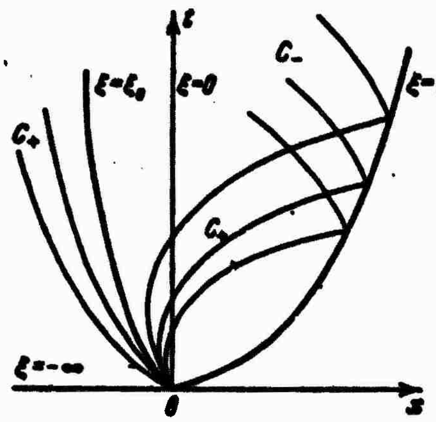

Fig. 12.13. x, t-diagram for the brief shock problem. $\xi = 1$ — line of front of shock wave, $\xi \equiv \xi_0$ — special ξ_0-line. Characteristics of the C_+- and C_--sets have been plotted.

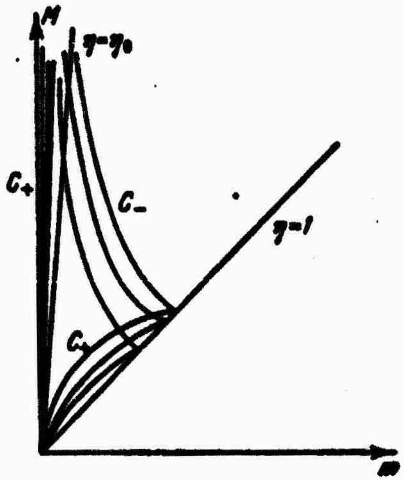

Fig. 12.14. m, M-diagram for the brief shock problem. $\eta = 1$ — line of front of shock wave, $\eta = \eta_0$ — special η_0-line. Characteristics of the C_+- and C_--sets have been plotted.

§ 16. Limitation of the Self-Similarity Exponent by the Laws of Conservation of Momentum and Energy

The character of motion which appears in a brief shock is such that some portion of the gas is attracted by the shock wave to the right, and the remaining gas scatters to the left into a vacuum.

There exists point which differentiates the shown portions of gas; we shall call the coordinate of this point x*. At point x* the mass speed of gas changes direction, i.e., is equal to zero, $u^* = u(x^*) = 0$. The actual boundary x* spreads in space and through mass to the right. In a self-similar solution, to the point of conversion of the sign of speed corresponds a certain defined value of the self-similar variable: $\xi = \xi^*$; $x^* = \xi^* X$.

Let us consider a volume included between the surface of the front of a shock wave x = X and the surface of "division" x = x*. This volume contains the mass (per cm^2 of surface):

$$M^* = \int_{x^*}^{X} \rho\, dx = \rho_0 X \int_{\xi^*}^{1} g\, d\xi = \text{const}'\, \rho_0 X.$$

It composes a fully determined portion of the total mass enveloped by motion $M = \rho_0 X$ (when $\gamma = 7/5$, $M^*/M = 0.78$). The remaining mass M - M* scatters to the left. Mass M*, just as total mass M, grows in time proportional to $M^* \sim X \sim t^{\alpha}$.

Boundary x* spreads through the mass to the right, i.e., the gas flows through the surface of x* to the left. Let us write the expression for momentum and energy of the gas which moves with the shock wave to the right:

$$I^* = \int_{x^*}^{X} \rho u\, dx = \rho_0 \dot{X} X \int_{\xi^*}^{1} g v\, d\xi = \text{const} \cdot t^{2\alpha-1}, \qquad (12.47)$$

$$E^* = \int_{x^*}^{X} \left(\frac{\rho u^2}{2} + \frac{p}{\gamma-1}\right) dx = \rho_0 \dot{X}^2 X \int_{\xi^*}^{1} \left(\frac{g v^2}{2} + \frac{\pi}{\gamma-1}\right) d\xi = \text{const} \cdot t^{3\alpha-2}. \qquad (12.48)$$

From the right, through the surface of the front of the shock wave, in the considered volume $x^* < x < X$, there flows an undisturbed gas with zero pressure and temperature. It does not introduce momentum or energy into the volume. From the left, through the surface of x^*, the gas leaves the volume with zero speed, but with finite pressure p^* (gas leaves the volume not by natural motion, but by the propagation of the surface which limits the volume). Momentum does not flow through the surface of x^*. Change of momentum in the volume is equal to the pressure applied to its boundary:

$$\frac{dI^*}{dt} = p^* > 0. \tag{12.49}$$

Momentum in the volume grows in time. From formula (12.47) it follows that $2\alpha - 1 > 0$, $\alpha > 1/2$, and by formula (12.41) $n < 2$.

Change of energy in the volume is determined only by the flow of internal energy through the left surface of x^*. Kinetic energy does not flow, since the speed of gas u^* and kinetic energy on boundary x^* are equal to zero. Work of the forces of pressure on the surface of x^*, p^*u^*dt, is also equal to zero. Consequently,

$$\frac{dE^*}{dt} = -\frac{1}{\gamma-1}\frac{p^*}{\rho^*}\rho^*\frac{dx^*}{dt} = -\frac{1}{\gamma-1}p^*\xi^*\dot{X} < 0. \tag{12.50}$$

Energy in the volume decreases in time, and flows from it to the left together with the mass of gas, which changes the direction of speed and starts to scatter to the left, into the vacuum. From formula (12.48) it follows that $3\alpha - 2 < 0$, $\alpha < 2/3$, and by formula (12.41) $n < 1$. Thus, we arrive at following limitations of the exponents of self-similarity:

$$\frac{1}{2} < \alpha < \frac{2}{3}, \quad 2 > n > 1. \tag{12.51}$$

Extreme values of $n = 1$ and $\alpha = 2/3$ correspond to the invariability of energy $E^* = \text{const}$, and extreme values of $n = 2$ and $\alpha = 1/2$

correspond to the invariability of momentum I* = const.

§ 17. Emergence of Nonself-Similar Motion Into Limiting Conditions and the "Infinity" of Energy in a Self-Similar Solution

A self-similar solution, strictly speaking, corresponds to idealized initial conditions, in which the duration of the shock τ is infinitely short, and pressure on the piston "during the shock" P_1 is infinitely long. Passage to the limit, $\tau \rightarrow 0$ and $P_1 \rightarrow \infty$, is accomplished in such a way that the product $P_1^{1/2}\tau^{1-\alpha}$, which is proportional to parameter A (see formula (12.36)), remains finite. In accordance with limiting values of $\tau \rightarrow 0$ and $P_1 \rightarrow \infty$, the piston imparts to the gas an infinite energy:

$$E \approx \rho_0^{-\frac{1}{2}} \Pi_1^{\frac{3}{2}} \tau \sim \tau^{-(2-3\alpha)} \longrightarrow \infty, \quad \alpha < \frac{2}{3}, \tag{12.52}$$

and zero momentum

$$I \approx \Pi_1 \tau \sim \tau^{2\alpha-1} \longrightarrow 0, \quad \alpha > \frac{1}{2}. \tag{12.53}$$

Let us compare energy E* and momentum I* of that portion of gas which moves to the right, in the direction of propagation of the shock wave (see formulas (12.47) and (12.48)) with energy E and momentum I of the entire gas on the whole. We have

$$\frac{E^*}{E} \sim \left(\frac{\tau}{t}\right)^{2-3\alpha}, \quad \frac{I^*}{I} \sim \left(\frac{t}{\tau}\right)^{2\alpha-1}, \quad \frac{1}{2} < \alpha < \frac{2}{3}. \tag{12.54}$$

Energy E* of a gas moving with the shock wave to the right, succeeds in decreasing to given moment t even a greater number of times as compared to initial energy E, the shorter the shock. Is not surprising that in the limit of vanishing short duration of shock $\tau \rightarrow 0$, infinite work of the piston is needed (infinite energy of gas E), so that, being reduced an infinite numer of times, the energy in a definite portion of mass remains finite. All this infinite energy is now concentrated in that portion of the mass which scatters into the vacuum; more exactly, on the very edge of the gas, which possesses infinite speed of scattering and infinite kinetic energy.

Unilateral momentum I* in a given moment of time is greater than the momentum of the piston I, the shorter the shock. In the limit $\tau \rightarrow 0$ unilateral momenta of parts of the gas, which move to the right and to the left, compensate one another with an accuracy of vanishing low magnitude of I.

Essentially, an idealized limiting solution corresponds not simply to zero duration of shock τ, but to an infinitely large ratio t/τ; $t/\tau \rightarrow \infty$ and $E^*/E \rightarrow 0$, $I^*/I \rightarrow \infty$.

Above, in the interpretation of this condition, we considered finite times t, but vanishing short times of shock τ, in accordance with which the work of the piston E was infinite, and momentum I was zero.

Nearer to reality is another interpretation of the limiting condition when not the duration of the shock tends to zero, but during an actually finite duration of shock and finite energy E there are considered times t that are large as compared to τ ($t/\tau \rightarrow \infty$ not because $\tau \rightarrow 0$, but because $t \rightarrow \infty$).

In examining the limiting conditions from such a point of view there appears the question of in what way does asymptotic transformation occur of a true motion, nonself-similar by virtue of the finiteness of τ, in limiting conditions? How does the infinity of energy of limiting motion agree with the actually finite work of the piston?

The fact is that the approximation of a true solution to a self-similar one occurs nonuniformly in time. With the growth of time t and mass of gas enveloped by motion $M = \rho_0 X$, pressure and all other magnitudes approach values corresponding to a self-similar solution.

However, such an approach does not occur everywhere.

In a certain mass m_0 near a boundary which, during a shock, was subjected to the direct influence of a piston, the state never approaches the one which is dictated by the self-similar solution. In order of magnitude this mass is equal to the mass of gas through which the shock wave passes during the actual shock: $m_0 \sim \rho_0 U_1 \tau \sim \sim \sqrt{P_1 \rho_0}\tau$.

The speed of scattering of this mass into a vacuum always remains finite and equal in order of magnitude to U_1 ($U_1 \sim \sqrt{P_1/\rho_0}$), when in the self-similar solution the speed of scattering of the boundary of gas is infinite (when $\tau \to 0$, $P_1 \to \infty$ and $U_1 \to \infty$). Entropy of mass m_0 is also finite, and is equal, by virtue of the adiabatic nature of motion, to initial entropy. Actually, $S = c_v \ln p\rho^{-\gamma} + \text{const}$. Magnitude $p\rho^{-\gamma}$ in mass m_0 in order of magnitude is equal to $P_1\rho_0^{-\gamma}$, i.e., it is limited at finite τ and P_1. In a self-similar solution with $\gamma = 7/5$, by formulas (12.42), we have

$$p\varrho^{-\gamma} \sim f g^{-\gamma} \sim \eta^{-\frac{4}{5}} \sim m^{-\frac{4}{5}} \to \infty$$

when $m \to 0$.

Thus, mass m_0 at the boundary forever carries the imprint of initial conditions and its state is not described by a self-similar solution even in the limit $t \to \infty$.

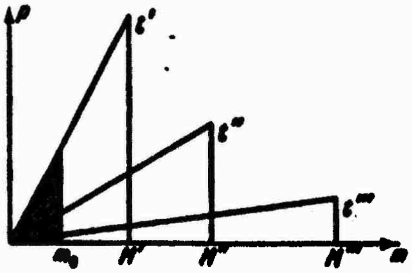

Fig. 12.15.

This position does not at all contradict the general tendency of a true solution to transform into a self-similar one in the limit $t \to \infty$. Mass m_0 in time composes a smaller and smaller portion of the entire mass of gas enveloped by motion (Fig. 12.15). In the limit $t \to \infty$ this small mass should not be considered in differential equations or in the convergent integral of momentum.

However, in the calculation of the integral of energy, the replacement in small mass m_0 of the true solution by a self-similar one leads to an essential change of the integral, and makes it divergent. In the self-similar solution the speed and kinetic energy of gas, during approach to the boundary $m \to 0$, tend to infinity, whereas in actuality, with finite pressure on piston P_1 and duration τ different from zero, the speed and kinetic energy of gas near the boundaries are finite.

In order to obtain finite energy of gas, actually responding to finite work of the piston, it is necessary, during the calculation of energy, with the help of the self-similar solution, to stop integration in that region where the self-similar solution is inapplicable.

We shall calculate energy by using Lagrange coordinates. Then, during integration of specific energy through the mass of gas enveloped by motion, as the lower limit we shall take the mass coordinate, in order of magnitude equal to mass m_0, which it is not described by the self-similar solution,

$$E=\int_{m_0}^{M}\left(\frac{u^2}{2}+\frac{1}{\gamma-1}\frac{p}{\rho}\right)dm=\rho_0\dot{X}^2X\int_{m_0/M}^{1}\left(\frac{v^2}{2}+\frac{1}{\gamma-1}\frac{\pi}{\delta}\right)d\eta.$$

Let us perform calculations for the case of $\gamma = 7/5$.

The main contribution to the integral is given by the region near the lower limit, where speed of gas and kinetic energy are very great (in limit $m_0/M \to 0$, $v \to -\infty$). Therefore, for calculation of the integral we shall use the asymptotic expression for speed (12.46) (see also (12.45).

We obtain $E\sim\rho_0\dot{X}^2X\int_{m_0/M}^{1}\eta^{-\frac{4}{3}}d\eta\sim\rho_0\dot{X}^2X\left(\frac{m_0}{M}\right)^{-\frac{1}{3}}.$

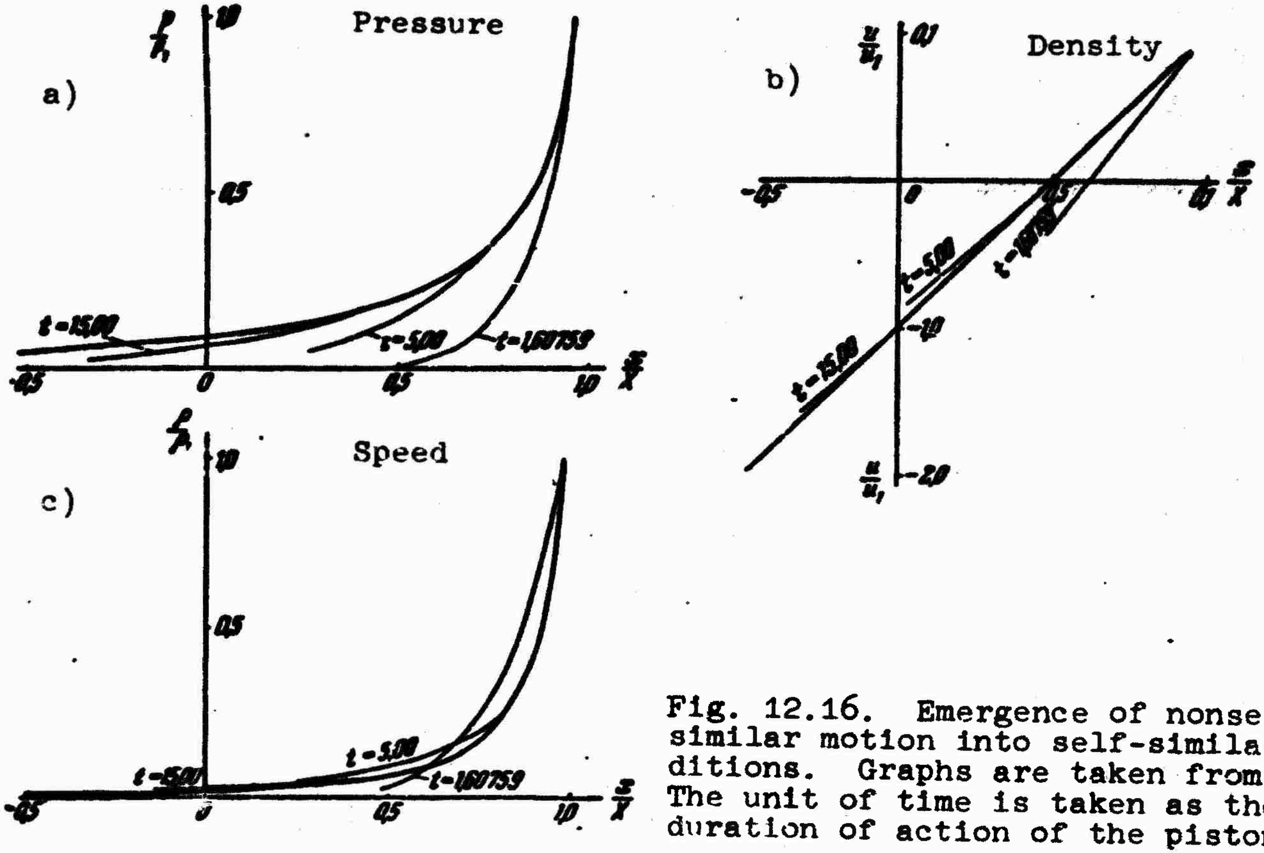

Fig. 12.16. Emergence of nonself-similar motion into self-similar conditions. Graphs are taken from [14]. The unit of time is taken as the duration of action of the piston τ.

Let us express the variables in this formula through X:

$$M = \rho_0 X;\quad \dot{X} = A^{\frac{5}{2}}X^{-\frac{3}{2}}\ \text{(Since } X = At^{\frac{2}{5}}\text{)}.$$

Considering the determination of $A \approx (P_1/\rho_0)^{1/2}\tau^{2/5}$ (formula (12.36)) and $m_0 \approx (P_1\rho_0)^{1/2}\tau$, we find that

$$E \sim \rho_0 A^{\frac{10}{3}} X^{-\frac{4}{3}} X m_0^{-\frac{1}{3}} \rho_0^{\frac{1}{3}} X^{\frac{1}{3}} = \rho_0^{\frac{4}{3}} A^{\frac{10}{3}} m_0^{-\frac{1}{3}} \approx \Pi_1^{\frac{3}{2}} \rho_0^{-\frac{1}{2}} \tau.$$

As can be seen, the energy of the entire mass of gas, with the exception of small mass m_0, to the self-similar solution which is inapplicable, is constant in time, is finite, and in order of magnitude is equal to the work of the piston.

Energy of the same order is also included in relatively small mass m_0. This mass flies into the vacuum with speed $- U_1$, having kinetic energy of the order $m_0 U_1^2 \approx \rho_0 U_1^3 \tau \approx \rho_0 (P_1/\rho_0)^{3/2}\tau \approx P_1^{3/2}\rho_0^{-1/2}\tau \approx E$. Within the confines of the self-similar solution in mass m_0 there is concentrated infinite energy, in spite of the fact that mass m_0 in time composes a smaller and smaller portion of the entire mass of gas enveloped by motion M.

It is essential that the region of gas, which is not described by the self-similar solution and which gives divergence in the integral of energy, if the self-similar solution is extrapolated by it, lies beyond the limits of the sphere of influence, to the left of the singular line, and in no way affects propagation of the shock wave. Actually, the boundary of the nonself-similar region is described by the equation $m \approx m_0$, and singular line $m = \eta_0 M$ ($m = 0.054\ M$ when $\gamma = 7/5$). When $t \to \infty$, $M \to \infty$ and $m_0 \ll \eta_0 M$.

In order to obtain a presentation of how nonself-similar motion emerges into limiting, self-similar conditions, the authors of [14] undertook the numerical calculation of equations of gas dynamics with

$\gamma = 7/5$ during a square pulse of piston pressure, shown in Fig. 12.9. Fig. 12.16 shows curves of the dependence of p/p_1, u/u_1, and ρ/ρ_1 on self-similar variable x/X for several moments of time (p_1, u_1, ρ_1, i.e., magnitudes of the front).

In the same place curves are plotted of an exact self-similar solution. As can be seen from the graphs, already when $t/\tau = 5$ the true solution is quite close to the self-similar one, and when $t/\tau = 15$, it almost coincides with the self-similar solution. Thus, the emergence of motion into self-similar conditions is carried out very fast. From the solution of the nonself-similar problem there can be found a numerical coefficient in expression (12.36) for parameter A. It turns out to be equal to 1.715, so that $A = 1.715(P_1/\rho_0)^{1/2}\tau^{2/5}$.

The numerical coefficient characterizes the form of momentum of piston pressure. It is possible to say that a square pulse is peculiar to the number 1.715 (when $\gamma = 7/5$).

§ 18. Concentrated Shock Along the Surface of a Gas (Surface Explosion)

Let us imagine a "spherical" analog of plane motion of gas during a brief shock along its surface. (Incidentally, we shall also consider a "cylindrical" case). This question was considered in the work of one of the authors of [20].

Let us assume that half-space $z > 0$ is occupied by an ideal gas with adiabatic exponent γ. Density of gas ρ_0 is constant and pressure is equal to zero. On the other side of plane $z = 0$, when $z < 0$, the space is empty. In initial moment $t = 0$ in a small mass of gas m, surrounding point 0 on boundary surface $z = 0$, a high energy E is quickly released. This can occur as a result of explosion on the surface or as a result of a "concentrated" shock along the surface by a fast "projectile" if the latter does not penetrate far into the depth of the substance, but is sharply decelerated near the surface. The kinetic energy of its motion is quickly turned into heat, i.e., there occurs somethind similar to an explosion.

From point O through the gas runs a shock wave. In the other direction the heated gas scatters into the vacuum. Initial speeds of gas both in the direction of propagation of the shock wave, and also in the direction of the vacuum are of the order $u_0 \sim \sqrt{E/m}$.*

The surface of the front of the shock wave, which is the surface of revolution around axis z, will form somethind like the "cup" shown in Fig. 12.17. Through the round "opening" of the cup (section in plane z = = 0) the gas, heated by the shock wave, flows from "cup" into the vacuum. Draining of gas weakens the shock wave as compared to the case when the "opening" is closed by a fixed "lid." This case would correspond to an explosion in an unlimited medium.

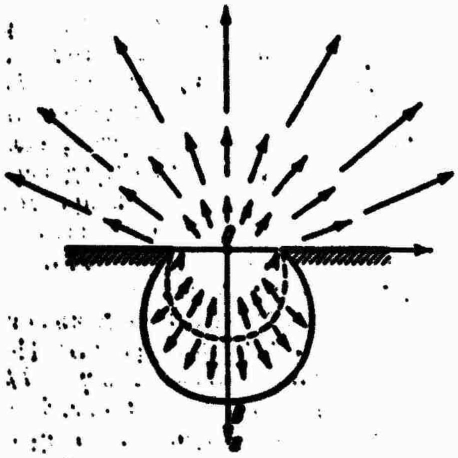

Fig. 12.17. Field of speeds during concentrated shock.

The shock wave moves the fastest of all downwards and the slowest of all along the surface z = 0, where it is greatly weakened due to expansion of the gas into the vacuum. Therefore, the surface of the front extends downwards as compared to a hemisphere. Near the front the gas moves in the direction of propagation of the wave. Somewhere inside the "cup" there passes a surface

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*If the cause of motion was the impact of a "projectile," m is the order of mass of the "projectile," E is the order of its kinetic energy, and u_0 is the order of impact speed.

on which the vertical component of speed changes direction. Above this surface, schematically shown in Fig. 12.17 by the dotted line, the gas moves in the direction of the vacuum (directions of speed are shown by arrows). With the departure from plane $z = 0$ in the earlier empty space $z < 0$ the speed of scattering increases, which is schematically shown in the figure by arrows of increasing length.*

It is quite evident that in the limit when the shock wave seizes mass $M \gg m$, the motion is self-similar. The surface of the front is then expanded, remaining similar to itself. The coordinate of any point of the front, let us say, point B, grows in time according to the law $z_1 \sim t^{\alpha}$. Pressure on the front (for instance, in that same point B) decreases with increase of mass M according to the law $p_1 \sim \sim M^{-n}$, whereby constants n and α are connected together by the simple relationship $n = 2(1 - \alpha)/3\alpha$.**

During a concentrated shock, exponent n, just as in the plane case, is limited by the inequality:

$$1 < n < 2. \tag{12.55}$$

In order to be convinced of this, we shall consider the stage at which $M \gg m$ and $p \sim M^{-n}$, and shall compose approximate expressions

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*Apparently, near the plane boundary of an undisturbed medium, the gas flowing from the "opening" moves along plane $z = 0$, and the pressure on the plane itself is equal to zero. It is possible that at certain values of γ there occurs breaking away, so that near plane $z = 0$ outside the "opening" there will form an empty conical slot. Perhaps, at certain γ the pressure on plane $z = 0$ outside the opening is finite, and near point A there appears a triple point. The front of the shock wave along plane $z = 0$ then spreads to infinity.

**$M \sim z_1^3 \sim t^{3\alpha}$. Speed of gas behind the front is proportional to $u \sim dz_1/dt \sim t^{\alpha-1} \sim \sqrt{p} \sim M^{-n/2} \sim t^{-3\alpha n/2}$. Hence: $\alpha - 1 = -3\alpha n/2$ or $n = 2(1 - \alpha)/3\alpha$.

for energy and vertical z-component of the gas momentum contained in the "cup." Taking the dimensional parameters into account in the proportionality factor between p and M, but without taking into account the numerical coefficient the average pressure with respect to the volume of the "cup" can be written in the form

$$p \sim \frac{E\rho_0}{m}\left(\frac{m}{M}\right)^n \sim p_0\left(\frac{m}{M}\right)^n. \qquad (12.56)$$

Here $p_0 \sim E\rho_0/m$ is the initial pressure at the time of impact ("explosion"). Average speed of gas in the "cup" in order of magnitude is equal to

$$u \sim \left(\frac{p}{\rho_0}\right)^{\frac{1}{2}} \sim u_0\left(\frac{m}{M}\right)^{\frac{n}{2}} \sim \left[\frac{E}{m}\left(\frac{m}{M}\right)^n\right]^{\frac{1}{2}}. \qquad (12.57)$$

Energy in the "cup" is of the order

$$E_1 \sim Mu^2 \sim \frac{Mp}{\rho_0} \sim E\left(\frac{m}{M}\right)^{n-1} \sim E_{10}\left(\frac{m}{M}\right)^{n-1}, \qquad (12.58)$$

where E_{10} is the initial energy in the "cup" which obviously is on the order of total energy E. Momentum in the "cup" is of the order

$$I_1 \sim Mu \sim \left[Em\left(\frac{m}{M}\right)^{n-2}\right]^{\frac{1}{2}} \sim I_{10}\left(\frac{m}{M}\right)^{\frac{n-2}{2}}, \qquad (12.59)$$

where $I_{10} \sim (Em)^{1/2}$ is the initial momentum.*

Energy flows from the "cup" through the "opening," since the speed of gas in the section of the "opening" is directed towards the vacuum. Consequently, energy E_1 contained in the "cup" decreases in time (with the growth of mass M), and by formula (12.58) $n > 1$.

The momentum of the gas in the whole "cup" shall be compared with the momentum of the part of it which is included between the surface of the front of the shock wave and the dotted surface where the vertical component of speed changes sign, i.e., is equal to zero.

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*In the case of impact of a "projectile" I_{10} of order of the momentum of the striking body.

Through this surface the momentum does not flow in vertical direction and the pressure on it is positive. Consequently, momentum grows with time, and by formula (12.59) $n < 2$. Vertical momentum of gas in the "cup" is balanced also by the increasing, but oppositely directed momentum of gas flowing from the "cup" and scattering into the vacuum. Thus, inequality (12.55) can be considered to be proven.* The value of $n = 1$ corresponds to conservation of energy in the "cup," i.e., an explosion in an unlimited medium. The value of $n = 2$ would correspond to the conservation of momentum.

The same inequality (12.55) is also valid in the "cylindrical" case or during "filamentary" impact. The pattern of motion during a "filamentary" impact (explosion) in the qualitative aspect is similar to the pattern, depicted in Fig. 12.17. Only now the explosion occurs not at point 0, but along a straight line passing through point 0 perpendicular to the plane of the figure. All motion is symmetric with respect to the plane passing through this straight line and axis z. The surface of the front will not form a "cup" but an infinitely long "ditch" whose cross section is depicted in the figure. M is the mass arriving per unit of length of the "ditch."

It is possible to establish an even narrower interval for the exponent in the law of damping of a shock wave. Physically, it is clear that with the same adiabatic exponent in the case of a concentrated shock, the wave is weakened with the growth of mass slower than in the plane case.

Actually, the weakening action of draining of gas from the front

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*Let us note that passage to the limit to self-similar conditions corresponds to $m \to 0$. So that pressure is finite, it is necessary that $Em^{n-1} \approx \text{const}$, i.e., that energy is infinite, $E \sim m^{-(n-1)} \to \infty$, and initial momentum is zero:

$$I_0 \sim (Em)^{\frac{1}{2}} \sim m^{2-n} \to 0.$$

is expressed smaller, the relatively smaller the area through which the gas flows into the vacuum. In the "spherical" case the area of the "opening" is much less than the surface area of the front of the shock wave (see Fig. 12.17). In the plane case both areas are equal. The "cylindrical" case is intermediate in this respect.

If we designate by n_1, n_2, and n_3 the exponents in the law of weakening of the shock wave $p \sim M^{-n}$ for plane, filamentary, and concentrated shocks correspondingly, then by virtue of what has been said, at the same adiabatic exponent

$$1 < n_3 < n_2 < n_1 < 2. \qquad (12.60)$$

For instance, when $\gamma = 7/5 n_1 = 4/3$ and $1 < n_3 < 4/3$. When $\gamma = 5/3$, $n_1 = 1.275$ and $1 < n_3 < 1.275$.

Thus, a concentrated shock is more like a localized explosion in an unlimited medium than a plane shock is like a plane explosion.

§ 19. Results of Simplified Consideration of Self-Similar Motion in Concentrated and Filamentary Impacts

In order to determine exponent $n(\gamma)$ in the law of damping of a shock wave $p \sim M^{-n}$, it is necessary, as in the plane case, to solve an equation of self-similar motion. However, "spherical" and "cylindrical" problems are incommensurably more complicated, since they are two-dimensional and self-similar motion is not described by ordinary differential equations, but by equations in partial derivatives. The position is essentially complicated even more by the fact that the surface of the front of the shock wave, to which the boundary conditions are assigned, is unknown beforehand and should be found in the course of the solution. For this reason even numerical integration of equations of self-similar motion should be connected with considerable difficulties.

A certain presentation about the numerical values of the exponent and general characteristics of motion is give by the simplified consideration of the problem conducted in [20]. An exact particular solution was constructed for differential equations of self-similar motion, which is a generalization of the exact solution of a one-dimensional problem (see § 15) and in certain respects correctly transmits the features of a two-dimensional process. The solution contains a series of unknown constants. It is clear that with the help of such a rather arbitrary particular solution of equations it is impossible to satisfy the boundary conditions on the front of a shock wave. Therefore, instead of the conditions on the front the solution was subordinated to general relationships, expressing in integral form the balances of mass, energy, and components of momentum of the gas contained in the "cup" (in the "ditch"). The form of the surface of the front was then selected as the most simple one. The "cup" was replaced by a circular cylinder with a "bottom" and the "ditch" with rounded shape by a "ditch" with a rectangular shape (Fig. 12.18).

Just as in the one-dimensional case, an exact analytic solution exists only at one (selected) value of adiabatic exponent γ (equal to 7/5), and also an approximate solution, which is a generalization of an exact one-dimensional one, is suitable only for one singular value of γ. This value together with the corresponding value of n is found in the solving process.

It turned out that in the case of concentrated impact $n = 1.07$ when $\gamma = 1.205$; the ratio of height of the "cylinder" h to diameter d is equal to 1.05; density of gas in the section of the "opening" is $\rho_{\text{open}} = 0.0187\rho_0$ and from the "opening" flow only 1.6% of the entire mass enveloped by the shock wave. Density of gas on the "bottom" of the cylinder is equal to $\rho_{bot} = 10.3$, which is very close to the actual density on the front of the shock wave $[(\gamma + 1)/(\gamma - 1)]\ \rho_0 = 10.7\rho_0$. The vertical component of speed changes direction at a depth of 0.846h from the "opening" and at a distance of 0.154h from the "bottom."

In the case of filamentary impact n = 1.14 when $\gamma = 1.266$, h/d = = 1.21 (h is the height of the "ditch" and d is the width), from the "ditch" flows 2% of the entire mass.

We see that exponents n turned out to be very close to unity, i.e., draining of gas from the front of the shock wave due to expansion of it into the vacuum only somewhat weakens the shock wave as compared to an explosion in an unlimited medium. This obviously is connected with the fact that beyond the limits of the "cup" ("ditch") a very small portion of the entire mass is ejected. The shape of the "cup" apparently essentially differs from hemispheric, which would correspond to an explosion in an unlimited medium. Height of the "cup," i.e., cylinder, is approximately equal to the diameter, whereas upon replacement of the hemisphere with an equivalent cylinder the height would be approximately two times less than the diameter. The same also pertains to a filamentary impact.

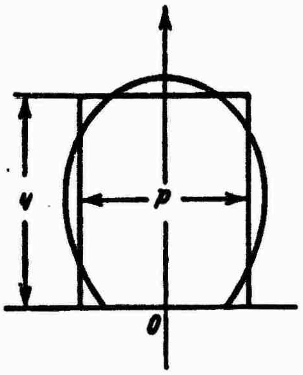

Fig. 12.18. Replacement of cup with an equivalent cylinder.

Fortunately, the adiabatic exponents $\gamma = 1.205$ and $\gamma = 1.266$, for which approximate solutions are suitable, are close to the real values of effective adiabatic exponents of gases at high temperatures, when the processes of dissociation and ionization are essential. Let us note that in the plane case the exponent n monotonically decreases with the growth of γ. If the same situation exists in two-dimensional cases, which is very probable, then for a concentrated impact $1 < n < 1.07$ when $\gamma > 1.205$, and for a filamentary impact $1 < < n < 1.14$ when $\gamma > 1.266$. In real processes, values of γ that are essentially smaller than 1.205 or 1.266 can scarcely present any interest. It follows from this that in the majority of real processes, a model of which could be the problem about the concentrated (or filamentary) impact, the shock wave attenuates only somewhat faster than in an explosion in an unlimited medium.

§ 20. The Impact After the Fall of a Very Fast Meteorite to the Surface of a Planet

A characteristic example of the phenomenon of "concentrated impact" could be the process occuring when a meteorite strikes the surface of a planet with a speed of the order of several tens or one hundred km/sec (and above). It is meaningful to consider either planets deprived of atmospheres, such as the moon, or rather large meteorites. Small meteorites evaporate and "burn" along the way due to the friction against the atmosphere, and never reach the surface of the planet.

When a meteorite strikes the ground there occurs a sharp deceleration and initial kinetic energy $E = mv^2/2$ (m is the mass of the meteorite, v is the rate of fall) in a considerable degree transfers into internal energy, into heat. The depth of penetration of the meteorite body into the ground is usually on the order of the dimensions of the body itself so that in the initial moment the energy release occurs in a mass of the order of m. From the place of energy release along the ground there spreads a shock wave.*

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*We do not consider impacts with low speeds, when an essential role is played the deceleration process itself, and propagation of the shock wave through the body of the meteorite is shorter when the energy release cannot be considered instantaneous.

We shall concern ourselves with impacts only with very high speeds, when specific energy $v^2/2$ many times exceeds the binding energy of atoms of molecules of the substances of the meteorite and the ground (heat of evaporation).

In this case there exists a stage when the shock wave envelopes a mass of ground M, considerably exceeding initial mass m, but the substance in the shock wave can be considered as a dense gas. The ground and the meteorite body during expansion are completely evaporated and scatter from the surface of the planet in a gaseous state. In the stage of not too strong expansion the pressure of the gas is much greater than atmospheric pressure and the existence of the atmosphere (if there is one) may be disregarded. Vapors are expanded just as into a vacuum. As can be seen, we are dealing with the typical picture of concentrated impact on the surface of the "gas" described in the preceding paragraph.

Let us estimate what is needed for this rate of fall. The heat of evaporation of iron (meteorites are of iron and rock) is equal to 94 kcal/mole = $7 \cdot 10^{10}$ erg/g. The heat of evaporation of rocks is about 83 kcal/mole = $5.8 \cdot 10^{10}$ erg/g. This value pertains to silica SiO_2, which is the basic component of different soils and rocks. If we consider also dissociation of SiO_2 molecules during evaporation, the binding energy will compose 203 kcal/mole = $1.4 \cdot 10^{11}$ erg/g.

For the estimation we shall say that for full evaporation it is necessary that specific energy 10 times exceeds the heat of evaporation, for which we shall take the tentative value of $U \approx 10^{11}$ erg/g. For the minimum speed at which a mass of the order of the meteorite mass, is evaporated we obtain the value of $v_{min} \approx \sqrt{2.10 \cdot 10^{11}} = 14$ km/sec. In exactly the same way it is possible to say that during propagation of a shock wave, completely evaporated during subsequent expansion are those layers of ground which the shock wave reached with specific internal energy ε_1 in the front of the order of $\varepsilon_k \sim 10U \sim 10^{12}$ erg/g.

Tenfold exceeding of ε_1 above U is taken on the basis of estimates in § 22, Chapter XI, where it was shown that full evaporation during unloading of a solid, compressed by a strong shock wave, is obtained if the energy in the front of the wave is at least one to five times greater than the binding energy of a crystal lattice.

In order to estimate the total mass of ground which is evaporated in the impact of a meteorite, it is necessary to use the law of damping of a shock wave. Such an estimate for the first time was made by K. P. Stanyukovich [21], who studied the phenomenon of "explosion" in the impact of a meteorite on the surface of a planet as the cause of the formation of craters on the moon. K. P. Stanyukovich did not take into account the effect of vapor scattering into the vacuum, assuming that a shock wave spreads exactly the same as in a strong explosion in an unlimited medium, i.e., according to the law $p_1 \sim M^{-1}$, $\varepsilon_1 \sim E/M$.

The consideration presented in the preceding paragraph are based on this assumption. Evaporated mass M_k in order of magnitude is determined by the relationship: $\varepsilon_k \sim E/M_k$, whence $M_k \sim E/\varepsilon_k \sim m\left(\frac{v^2}{\varepsilon_k}\right) =$ $= m(v/v_k)^2$, where $v_k = \sqrt{\varepsilon_k} \sim 10$ km/sec. For instance, with a meteorite speed of $v \sim 100$ km/sec there is evaporated a mass of ground that 100 times exceeds the mass of the meteorite.

When the energy in the shock wave becomes less than $\sim 10^{12}$ erg/g, the layers of the ground captured by the wave no longer are evaporated during unloading. However, the energy in the wave is still fully sufficient for mechanical breaking of the substance. The limiting energy necessary for destruction is much less than the heat of evaporation. Therefore, the mass of a crushed substance many times exceeds the mass of an evaporated substance. The crushed substance is ejected upwards in the form of solid particles, and in this way there appears a crater. Questions about the dimensions of the crater after the impact of a meteorite, the role of gravity, which prevents remote scattering of the substance, and others, were considered by K. P. Stanyukovich [21].

Effects similar to an "explosion" in the impacts of fast meteorites also appear during motion in a rarefied atmosphere of body with very great speed. Impacts of molecules of air against the surface of the body are like the impacts of meteorites against the surface of planets. In every impact there occurs a "microexplosion" and from the surface of the body there is ejected a certain quantity of evaporated substance. The body obtains an additional impulse of recoil, which leads to an increase of the drag factor and an increase of the speed of braking of the body in the atmosphere. This phenomenon is considered in the work of K. P. Stanyukovich [22]. The impact of a fast body on a liquid surface, on assumption of its incompressibility, was considered by M. A. Lavrent'yev [23].

§ 21. A Powerful Explosion in an Unlimited Porous Medium

In the work of A. S. Kompaneyets [24] the problem is solved for a powerful localized explosion in a plastic packing medium with continuous packing on the front of the shock wave.* We shall consider here a simplified problem about the propagation of the shock wave of a localized explosion in a porous medium under the condition that the

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* In [25] the packing is assumed to depend on the amplitude of the wave.

solid substance is incompressible (for instance, in sand with incompressible sand grains). Strength of the sand grains will be disregarded, i.e., we shall consider that for adiabatic compression of the material to the density of the solid substance (for full "selection" of vacuums) no expenditure of energy is required. In other words, the shock wave is considered to be powerful with respect to the strength of the material, but weak with respect to elasticity (compressibility of the solid substance). Initial pressure p_0 is equal to zero.

Let us designate average density of an undisturbed medium by ρ_0, and density of the solid substance ("sand grains") by ρ_1; $\rho_0 = \rho_1(1-k)$, where k is the coefficient of porosity, which can vary from zero to one.

Let us assume that at a certain point there occurs a strong "explosion"; the substance is given an intense initial shock, for instance, the spherical "piston" expanded and stopped quickly. Through the substance there will pass a shock wave in which the material will be compressed to the density of the solid substance with complete filling of vacuums. After that, the density of the substance no longer changes and remains equal to ρ_1. The substance, seized by the shock wave, moves behind the front. Near the surface of the front there will form a spherical shell of constant density ρ_1, and behind it an empty cavity, as shown in Fig. 12.19a.

If the radius of the front of the wave is R, and the radius of the internal surface of the layer is r_c, the condition of conservation of mass gives:

$$M = \frac{4\pi}{3} R^3 \rho_0 = \frac{4\pi}{3}(R^3 - r_c^3)\rho_1,$$

or

$$r_c^3 = R^3\left(1 - \frac{\rho_0}{\rho_1}\right) = R^3 k. \qquad (12.61)$$

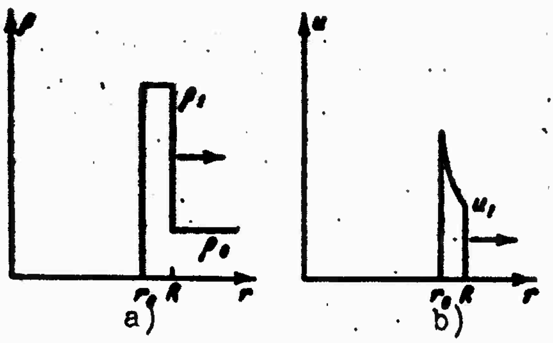

Fig. 12 19. Distributions of density (a) and speed (b) along the radius during an explosion in sand with incompressible sand grains.

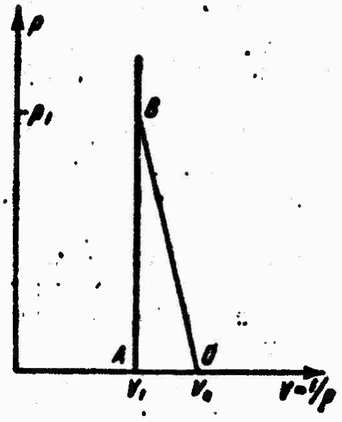

Fig. 12 20. Shock adiabat of sand with incompressible grains without taking into account strength.

Distributions of speed in the layer follows from the continuity equation for an incompressible fluid: div u = 0,

$$u = u_1\left(\frac{R}{r}\right)^2, \quad r_0 < r < R, \tag{12.62}$$

where u_1 is the mass speed behind the front of the shock wave (see Fig. 12.19b). It is connected with the speed of the front D = dR/dt by an evident relationship:

$$u_1 = D\left(1 - \frac{\rho_0}{\rho_1}\right) = Dk. \tag{12.63}$$

The shock adiabat of the substance under the assumptions made in the beginning has the form shown in Fig. 12.20.* Let us assume that the "pressure" in the shock wave is equal to p_1 (point B on the shock adiabat). As it is known (see § 16, Chapter I), the initially stationary substance in a strong shock wave ($p_1 >> p_0$) obtains identical kinetic and internal energy $u_1^2/2$ per gram. Numerically these energies

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*For shock compression of porous material taking into account compressibility of solid substance see § 10, Chapter XI.

are equal to the area of triangle OAB in Fig. 12.20. Inasmuch as solid particles are assumed to be incompressible, the fate of the internal energy obtained by the substance in the shock wave does not interest us. This energy is turned into heat and constitutes simply a loss of mechanical energy of motion. Thus, a decrease of kinetic energy of the entire mass M during the time dt is equal to an increase of internal energy of mass dM, which is seized by the shock wave during the time dt:

$$-d\left(\frac{M\overline{u^2}}{2}\right)=-\beta d\left(\frac{Mu_1^2}{2}\right)=\frac{u_1^2}{2}dM. \tag{12.64}$$

Here, $\overline{u^2} = \beta u_1^2$ designates the mean square of speed of mass M. Coefficient β is easy to calculate with the help of equations (12.62) and (12.61): $\beta = 3/(k + k^{2/3} + k^{1/3})$. Integration equation (12.64), we find the law of damping of the shock wave:

$$u_1^2=\text{const}\cdot M^{-(1+\beta)/\beta}=\text{const}\, M^{-n}. \tag{12.65}$$

Here, by analogy with the preceding sections, we designated the exponent of mass in the formula for specific energy by n : $n = (1+\beta)/\beta$. Full kinetic energy of motion is proportional to $E_k = \frac{M\overline{u^2}}{2} \sim M^{-(n-1)}$; momentum is $I \sim Mu_1 \sim M^{1-n/2}$. Inasmuch as $\beta > 0$, exponent n is always included in the limits of $1 < n < 2$ (see results of § 18). In the limiting case of a solid incompressible medium $k \to 0$, $\beta \to \infty$, $n \to 1$, energy is conserved, and momentum grows in time. In the limiting case of an extraordinarily porous substance (strongly "compressible" medium) $k \to 1$, $\beta \to 1$, $n \to 2$, momentum is conserved, but energy decreases. In the general case of $0 < k < 1$ energy decreases (passes into heat) and momentum grows. The position, as we can see, is the same as in the impact on the surface of a gas (see § 18).

As in the limiting case of a "localized" explosion, the initial energy is infinite (if $k \neq 0$, $n > 1$, and $E_k \sim M^{-(n-1)} \to \infty$ when $M \to 0$).

§ 22. Self-Similar Motion in a Nonhomogeneous Atmosphere Caused by a Brief Plane Shock

Let us assume that the density of a gas is distributed in space according to exponential (barometric) law

$$\rho_0 = \rho^0 e^{x/\Delta}, \tag{12.66}$$

where the scale of length Δ is constant. This is the distribution of air density with respect to height (axis x is directed downwards) on the assumption that temperature in the atmosphere is identical everywhere. Distribution (12.66) possesses the property that the mass of gas, concentrated in a column of unitary section, from $x = -\infty$, where $\rho_0 = 0$, and to $x = X$, is equal to the mass of gas in a column with length Δ, if the density in it is equal to $\rho_0(X)$

$$M = \int_{-\infty}^{X} \rho_0(x)\,dx = \rho_0(X)\,\Delta. \tag{12.67}$$

Let us assume that at initial moment $t = 0$, somewhere in the region of very small density, when $x \approx -\infty$, there is produced a brief plane shock. Through the gas in the direction of growth of density there will run a shock wave, but the heated gas will be expanded in the direction of the vacuum.

We shall find limiting motion in the stage when the shock wave envelopes the mass of gas M, which is much larger than mass m_0 in the region of small density, subjected to the intial action of the shock. Initial pressure of gas will be considered to be equal to zero. As can be seen, formulation of the problem is fully analogous to the formulation of the problem of the brief shock along the surface of a gas of constant density bordering on a vacuum (see § 13). The problem of the brief shock in the case of a nonhomogeneous atmosphere was formulated and solved in the work of one of the authors [28]. (In the following paragraph it will be shown what real process it describes).

It is clear that the limiting motion ($M \gg m_0$) is self-similar. However, this self-similarity has a somewhat unusual character. The fact is that in distinction from all other considered self-similar motions, in conditions of the problem there is a scale of length Δ, but there is no parameter, the dimension of which would contain the symbol of mass (usually such a parameter exists in connection with the assignment of initial density of gas). Magnitude ρ^* in (12.66) cannot serve as a parameter, since it is indefinite because of arbitrary character of selection of the beginning of reading of coordinate x).*

Coordinate x is determined only with an accuracy of additive constant; therefore, motion can depend only on the difference of coordinates, but not on the actual coordinate x. The difference of coordinates is the distance counted off from the front of the shock wave, the coordinate of which will be designated as X, so that motion depends on the dimensionless distance

$$\xi = \frac{X - x}{\Delta}. \tag{12.68}$$

This magnitude is also a self-similar variable, where, in distinction from all other considered self-similar motions, the self-similar variable does not contain time. (Motion of course is peculiar to a certain parameter A, characterizing "shock strength"; however, due to the absence of another parameter, the dimension of which would contain the symbol of mass, from magnitudes X, A, and Δ it is impossible

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*ρ^* is the density at point $x = 0$, but the origin, $x = 0$, we place to the right of the point with any density.

to compose a combination of the dimension of time and, consequently, from the independent variables and parameters x, t, A, and Δ it is impossible to compose a dimensionless variable which could contain time t).

After the remarks made about the dimension properties of the problem and the uncertainty of coordinate x it is easy to find the law of motion of the shock wave and to write general expressions for the unknown functions: speed, pressure, and density.

Speed of the front of the of the shock wave is equal to

$$D=\dot{X}=\alpha\frac{\Delta}{t}, \tag{12.69}$$

where the numerical coefficient α depends only on adiabatic exponent γ. The coordinate of the front X grows in time by logarithmic law:

$$X=\alpha\cdot\Delta\ln t+\text{const.} \tag{12.70}$$

Expressions for speed, density, and pressure of gas behind the front of the shock wave have the form

$$\left.\begin{aligned} u&=u_0\tilde{u}=\frac{2}{\gamma+1}\alpha\frac{\Delta}{t}\tilde{u},\\ \rho&=\rho_0\tilde{\rho}=\frac{\gamma+1}{\gamma-1}\rho_0(X)\tilde{\rho},\\ p&=p_0\tilde{p}=\frac{2}{\gamma+1}\alpha^2\frac{\Delta^2}{t^2}\rho_0(X)\tilde{p}, \end{aligned}\right\} \tag{12.71}$$

where the dimensionless representative functions $\tilde{u}$, $\tilde{\rho}$, and $\tilde{p}$ depend on the self-similar variable ξ, i.e., the dimensionless distance counted off from the front of the shock wave, and γ. The representative functions are determined in such a way, that on the front of the shock wave, when $\xi = 0$, they all become one

$$\tilde{u}(0)=\tilde{\rho}(0)=\tilde{p}(0)=1. \tag{12.72}$$

Another boundary condition consists of the fact that a "vacuum" when $x = -\infty$, $\xi = \infty$, and $\tilde{p}(\infty) = 0$.

The density of the gas directly before the front of the shock wave $\rho_0(X)$ is expressed by the mass coordinate of the front M by formula (12.67).

The mass of gas enveloped by the shock wave, in distinction from the geometric coordinate, as usual depends on time according to root law $\dot{M} = \rho_0(X)\dot{X} = M\dot{X}/\Delta = M\alpha t^{-1}$, whence

$$M = At^{\alpha}. \tag{12.73}$$

Here A is the constant of integration, which is also the parameter characterizing the "shock strength." Its size is $[A] = g \cdot cm^{-2} \cdot sec^{-\alpha}$.

Thus, in formulas (12.71) it is possible to place the evident dependence of $\rho_0(X)$ on time

$$\rho_0(X) = \frac{M}{\Delta} = \frac{At^{\alpha}}{\Delta}. \tag{12.74}$$

The motion, as already was noted above, possesses an unusual self-similarity: profiles of speed, density, and pressure as if are "attached" to the front of the shock wave and move together with the front, not extending with the passage of time (only the amplitudes of these magnitudes change). However, in Lagrange coordinates the motion is self-similar in the usual sense. Lagrange coordinate m is equal to

$$m = \int_{-\infty}^{x} \rho(x)\,dx = \text{const} \cdot M \int_{\xi}^{\infty} \tilde{\rho}(\xi)\,d\xi,$$

i.e., ξ, and consequently, $\tilde{u}$, $\tilde{\rho}$, and $\tilde{p}$ are functions of self-similar variable $\eta = m/M = m/At^{\alpha}$.

Equations of self-similar motion are conveniently solved in Lagrange coordinates. Let us place expressions (12.71) and (12.74) in corresponding equations of gas dynamics

$$\frac{\partial u}{\partial t} + \frac{\partial p}{\partial m} = 0, \quad \frac{\partial (1/\rho)}{\partial t} - \frac{\partial u}{\partial m} = 0, \quad p\rho^{-\gamma} = F(m).$$

Let us obtain equations for representative functions $\tilde{u}(\eta)$, $\tilde{\rho}(\eta)$, and $\tilde{p}(\eta)$:

$$\left.\begin{array}{c}\tilde{u}+\alpha\eta\tilde{u}'=\alpha\tilde{p}'; \quad \frac{1}{\tilde{\rho}}+\eta\left(\frac{1}{\tilde{\rho}}\right)'=-\frac{2}{\gamma-1}\tilde{u}'; \\ \tilde{p}\,\tilde{\rho}^{-\gamma}\eta^{\frac{2}{\alpha}+\gamma-1}=1.\end{array}\right\} \qquad (12.75)$$

Integrating the second equation and excluding from the system $\tilde{\rho}$ and $\tilde{u}$, we obtain a fundamental equation of the problem

$$\frac{d\tilde{p}}{d\eta}=\frac{\gamma+1}{2\alpha}\cdot\frac{1-\frac{\gamma-1}{\gamma+1}\left(1-\frac{2-\alpha}{\gamma}\right)\tilde{p}^{-\frac{1}{\gamma}}\eta^{-\frac{2-\alpha}{\alpha\gamma}}}{1-\frac{\gamma-1}{2\gamma}\tilde{p}^{-\frac{1}{\gamma}-1}\eta^{1-\frac{2-\alpha}{\alpha\gamma}}}. \qquad (12.76)$$

The solution of $\tilde{p}(\eta)$ should pass through two points $\tilde{p}(1) \ll 1$ and $\tilde{p}(0) = 0$, which also determines exponent α.

In the particular case of $\gamma = 2$ it is possible to find an exact analytic solution of the problem. We have:

$$\begin{array}{c}\alpha=\frac{3}{2}, \quad M\sim t^{2/3}, \quad D=\frac{3}{2}\frac{\Delta}{t}; \quad u_\phi\sim\frac{1}{t}, \quad \rho_\phi\sim t^{2/3}, \quad p_\phi\sim\frac{1}{t^{4/3}}; \\ \tilde{p}=\eta, \quad \tilde{\rho}=\eta^{5/3}, \quad \tilde{u}=\frac{3}{2}\left(1-\frac{1}{3}\eta^{-2/3}\right)^{*)}.\end{array} \qquad (12.77)$$

In Euler coordinates the solution has the form:

$$\tilde{p}=(1+2\xi)^{-3/2}, \quad \tilde{\rho}=(1+2\xi)^{-5/2}, \quad \tilde{u}=1-\xi. \qquad (12.78)$$

An analytic solution is also possible when $\gamma = 1$: $\alpha = 1$, $\tilde{p} = \eta$, $\tilde{\rho} = \eta^3$, and $\tilde{u} = 1$. This case presents interest only from the point of view of limitation of the exponent of self-similarity α, since it corresponds to infinite compression of gas in the front of the wave, as a result of which in Euler coordinates $\tilde{p}$, $\tilde{\rho}$, and $\tilde{u}$ become a

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*The solution in Lagrange coordinates is absolutely analogous to the analytic solution of the usual problem of a brief shock in the case of $\gamma = 7/5$. (See (12.42)).

δ-function: $\delta(\xi)$

Inasmuch as the real values of γ are included in the range $1 < \gamma < 2$, we must assume that the corresponding values of the exponent of self-similarity lie in the interval $1 < \alpha < \frac{3}{2}$.*

At an arbitrary value of γ the solution can be found by means of numerical integration of equation (12.76) by the trial-and-error method.

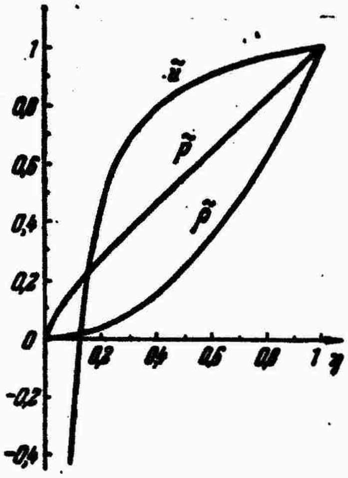

Fig. 12.21. Distributions of speed $\tilde{u}$, pressure $\tilde{p}$, and density $\tilde{\rho}$ along the mass coordinate.

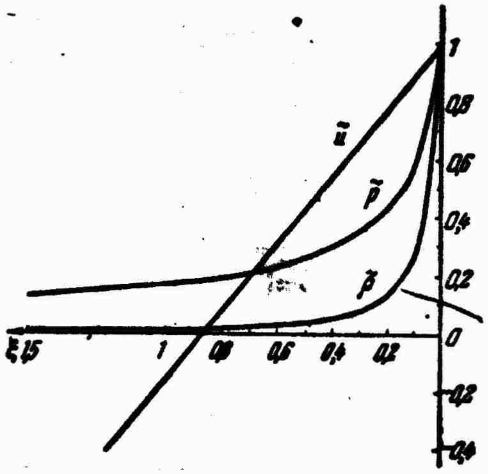

Fig. 12.22. Distributions of speed $\tilde{u}$, pressure $\tilde{p}$, and density $\tilde{\rho}$ in the space behind a shock wave.

Figs. 12.21 and 12.22 give the thus obtained distributions of speed, density, and pressure along the mass and in space for $\gamma = 1.25$. Exponent α is equal to $\alpha = 1.345$.

§ 23. Propagation of a Shock Wave Downwards During an Explosion in a Nonhomogeneous Atmosphere

Section 28, Chapter I considered how a shock wave is propagated during a strong explosion in a nonhomogeneous, exponential atmosphere. The law of motion of the shock wave was approximately found in the work

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*Consideration of balances of energy and impulse, analogous to that conducted in § 16, leads to the general limitation $1 < \alpha < 2$.

of A. S. Kompaneyets [29] and was somewhat definitized in the work of E. I. Andriankin, A. M. Kogan, A. S. Kompaneyets, and V. P. Kraynov [30].

The chief characteristic of motion consists in that the shock wave is weakened during motion in various directions unequally. During motion downwards, in the direction of increase of density, it is delayed the fastest of all. Conversely, during upward motion, in the direction of decrease of decrease of density, the wave even accelerates and in a finite period of time it departs upwards to an infinite distance, as if "breaking through" the atmosphere. The surface of the front of the shock wave will form something like a "cup" and in the huge cavity limited by this surface the pressure drops to a very small magnitude. The method of approximation [29, 30] does not describe the process any further.

In a strong explosion in a homogeneous atmosphere the pressure in the volume is equalized and is less than the pressure on the front of the shock wave by a total of two or three times (depending upon adiabatic exponent; see §§ 25 and 26, Chapter I). This internal pressure "supports" the shock wave and promotes the fact that the wave attenuates slower than in the absence of internal pressure. The role of internal pressure is especially distinct if we compare the motion during a plane explosion with the motion during a plane brief shock, when pressure behind the front of the shock wave decreases to zero and there is no internal pressure supporting the wave. The shock wave in this last case attenuates faster.

But in an explosion in a nonhomogeneous atmosphere, due to the sharp fall of pressure in the cavity with the increase of its volume, the position in some measure is like what takes place in the problem of the brief shock. Internal pressure no longer supports the shock wave spreading downwards, and the gas flows from the front, rushing upwards into the "empty" cavity.

Thus, when pressure in the cavity p_c becomes much less than the pressure on the front of the shock wave p_f, the motion of the shock wave downwards obtains the features of motion described in the preceding paragraph (curvature of the front in order of first approximation can be disregarded). (Incidently, under the condition of $p_f \gg p_c$ the solution also loses force [29, 30]. Numerical estimates show that pressure in the cavity becomes much less than the pressure on the front, when the speed of the front is still sufficiently great that in examining the subsequent motion the counterpressure in the direction of undisturbed air still may be disregarded.

We shall assume for definitiveness that the transition to a new regime occurs when $p_f/p_c = 10$. According to [30] this value corresponds to the time from the moment of explosion $t_1 = 19\tau$, where $\tau = (\rho_{00}\Delta^5/E)^{1/2}$ is the scale of time that is characteristic for an explosion in a nonhomogeneous atmosphere (ρ_{00} is the air density at the height of the explosion, E is the energy of the explosion). To moment t_1 the shock wave departs downwards from the point of explosion to distance $z = 1.9\Delta$; speed of the front is then equal to $D_1 = 2.5 \times 10^{-2} \times \Delta/\tau$.

We shall extrapolate the limiting laws of propagation of the shock wave (12.69), (12.70) to the moment of "transition" to the new regime, where upon the coordinate and time will be counted off in such a way that the initial condition of $D = D_1$ when $X = 0$ is fulfilled.*

---

*The process up to the moment of "transition" plays the role of the "brief shock."

Let us obtain an approximate dependence of the coordinate of the front on the speed of the front and on time (the coordinate is counted off downwards from the point of "transition" to the new regime):

$$X = \alpha \cdot \Delta \ln \frac{D_1}{D} = \alpha \Delta \ln \frac{t}{\theta}.$$

Parameters D_1 and θ are determined through the parameters of the explosion by expressions $D_1 = 2.5 \cdot 10^{-2} \frac{\Delta}{\tau} = 2.5 \cdot 10^{-2} \left(\frac{E}{\rho_{00} \Delta^3} \right)^{1/2}$;* $\theta = 40\, \alpha\tau$; $\alpha = 1.345$ when $\gamma = 1.25$. Impact parameter A in the same approximation is equal to $A = e^{1.9} \rho_{00} \Delta \theta^{-\alpha} = 6.7 \rho_{00} \Delta \cdot \theta^{-\alpha}$.

An estimate with the help of the real numerical values of parameters shows that in the process of deceleration of the shock wave from "transition" speed D_1 to speed $D \approx 1$ km/sec, a few times exceeding the speed of sound in cold air, the shock wave covers a distance downwards of approximately (2 to 3)Δ.

It is added to a distance of about 2Δ downwards from the center of the explosion, which follows from the theory in [29, 30]. Thus, in the process of deceleration of the shock wave of a strong explosion to a speed of the order of 1 km/sec, the wave covers a distance downwards from the point of explosion of about (4 to 5)Δ.

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*The numerical values of parameters D_1 and θ weakly depend on the selection of the transition value of p_f/p_c. Thus, for instance, in the latter, calculated in [30], moment $t = 23.4\tau$, close to the moment of "breakthrough" of the atmosphere, $z \approx 2\Delta$, $D = 2.12 \cdot 10^{-2}\ \Delta/\tau$, $p_f/p_c = 22$.

Literature

1. K. P. Stanyukovich. Transient motions of a solid medium, State Technical Press, 1955.

2. L. I. Sedov. Methods of similarity and dimension in mechanics, State Technical Press, 4th Edition, 1957.

3. G. Guderley. Luftfahrtforschung, 19, 302 (1942).

4. Rayleigh. Phil. Mag., 34, 94 (1917).

5. C. Hunter. J. Fluid Mech., 8, 241 (1960).

6. Ye. I. Zababakhin. Applied Mathematics and Mechanics, 24, 1129 (1960).

7. D. A. Frank-Kamenetskiy. DAN SSSR, 80, 185 (1951).

8. G. M. Gandel'man and D. A. Frank-Kamenetskiy. DAN SSSR, 107, 811 (1956).

9. A. Sakurai. Communic. on Pure and Appl. Math., 13, 353 (1960).

10. V. L. Ginzburg and S. I. Syrovatskiy. UFN, 71, 411 (1960).

11. S. A. Colgate and M. H. Johnson. Phys. Rev. Letters, 5, 235 (1960).

12. Ya. B. Zel'dovich. Acoustical Journal, 2, 28 (1956).

13. V. B. Adamskiy. Acoustical Journal, 2, 3 (1956).

14. A. I. Zhukov and Ya. M. Kazhdan. Acoustical Journal, 2, 352 (1956).

15. W. Häfele. Z. f. Naturforschung, 10a, 1006 (1954).

16. S. Hoerner. Z. f. Naturforschung, 10a, 687 (1955).

17. C. Weizsacker. Z. f. Naturforschung, 9a, 269 (1954).

18. V. B. Adamskiy and N. A. Popov. Applied Mathematics and Mechanics, 23, 564 (1959).

19. N. L. Krasheninnikova. News of Academy of Sciences USSR, No. 10, 14 (1955).

20. Yu. P. Rayzer. PMTF, No. 1 (1963).

21. Second Conference on Cometary and Meteoric Astronomy, Astronomical Journal, 14, No. 3, 249 (1937); K. P. Stanyukovich and V. V. Fedynskiy, DAN SSSR, 57, No. 2 (1947); K. P. Stanyukovich , Meteoritics, No. 7 (1950); Artificial Earth Satellites, No. 4, 86 (1960).

22. K. P. Stanyukovich. News of Academy of Sciences USSR, OTN, Mechanics Machine Buildings, No. 5, 3 (1960).

23. M. A. Lavrent'yev. Artificial Earth Satellites, No. 3, 61 (1959).

24. A. S. Kompaneyets. DAN, 109, No. 1 (1956).

25. E. I. Andriankin and V. P. Koryavov. DAN, 128, 257 (1959).

26. Ya. B. Zel'dovich. ZhETF, 33, 700 (1957).

27. Ye. I. Zababakhin and M. N. Nechayev. ZhETF, 33, 442 (1957).

28. Yu. P. Rayzer. DAN SSSR (1963) (in press).

29. A. S. Kompaneyets. DAN SSSR, 130, 1001 (1960).

30. E. I. Andriankin, A. M. Kogan, A. S. Kompaneyets, and V. P. Kraynov. PMTF, No. 6 (1962).

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