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THEORY OF EXPLOSIVE SUBSTANCES

By

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THEORY OF EXPLOSIVE SUBSTANCES.

By: K. K. Andreyev and A. F. Belyayev

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TABLE OF CONTENTS

APPENDICES

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
Й й	*Й й*	Y, y	Щ щ	*Щ щ*	Shch, shch
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 yё or ё. 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

The basic physicochemical properties, of explosives are discussed ~~in the book. T~~hese properties are essential for the production of explosives are discussed. Application of the theory of slow thermal transformation, combustion and detonation of explosives and the destructive effects of explosion are also d~~iscussed~~ [illegible]. ~~in the book~~.

The book is intended for students of corresponding departments of higher chemico-technological educational institutions, and also for workers of factories and scientific research institutes.

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PREFACE

The course on the theory of explosives is included in the educational plan of the corresponding specialities of higher chemico-technological educational institutions and military academies.

Books by N. A. Sokolov "Course on theory of explosives" and K. K. Snitko "Theory of explosives," published in 1936-1937, reflected deeply and sufficiently the state of the above science.

During the years that have lapsed since the publication of these textbooks, and especially on the basis of the great Patriotic war experiment, knowledge of explosives and explosions was enriched by new data and resulted in greater development of the field.

In our literature, as well as the publications abroad, these achievements at that time were generalized and were explained insufficiently. This pertains especially to the literature of scientific education.

The authors attempted to close the gap on questions of the theory of explosives, in reference to programs of higher chemico-technological educational institutions.

In accordance with the main purpose of the book; questions pertaining to the effect of explosions, in particular, explosion of ammunitions, are illuminated relatively consicely. In this section the course is short. At the same time, in order to present a possibility to readers to expand and to deepen somewhat their knowledge information is given in small type in certain sections as an obligatory minimum, foreseen in educational program. Reference data given in the form of appendix at the end of the book serves the same purpose.

The book consists of 10 chapters.

The main regions for using the energy of explosion in technology and also the theoretical problems of explosive substances (E.S.) are discussed briefly in the introduction.

In Chapter I are given basic determinations of explosion phenomenon in different forms and those conditions at which chemical transformation can take character of explosion.

Chapter II deals with the simplest of the three basic forms of chemical reactions which take place in E.S. — slow chemical transformation.

In Chapter III the question of stability of E.S., important in technology is considered, in particular, the experimental methods for determination of stability.

In Chapter IV a description is given for basic forms of self-propagating chemical transformation — combustion and detonation. The application of E.S. is based on their use. Theory of these phenomena is also considered in this chapter.

Chapter V deals with the excitation of combustion and detonation of E. S. at various influences on them.

In Chapter VI are considered basic regularities of propagation in air and in other media of shock waves, which appear during the explosion and determine its destructive effect

Chapter VII deals with questions on the composition of explosion products and factors which at various conditions can affect this composition.

In Chapter VIII are considered methods of determination of heat, temperature and volume of gases during the explosion, i.e., those characteristics, on which the destructive effect depends. Basic forms of this effect, methods of their evaluation and the relation of these forms with the properties of explosives are described in Chapter IX.

The last chapter of the book, Chapter X, deals with the theory of ignition of methane-air and dust-air mixtures from the explosion ES. This theory is the basis for the creation of special safety explosives intended for coal mines and development of other measures, which ensure the safety of blasting in these mines.

Chapters VI and IX of the book and also sections of Chapter IV, dealing with the detonation theories in gases (pp. 320-351), experimental methods of determination of speed and pressure of detonation (pp. 302-319 and 356-359), and also critical diameter (pp. 283-286) are written by A. F. Belyayev. The remaining chapters are written by K. K. Andreyev.

Authors express sincere gratitude to comrades and specialists in the field D. S. Avanesov, A. Ya. Apin, A. I. Gol'binder, L. V. Dubnov, A. A. Zaytsev, A. M. Lomovoy, K. K. Snitko, I. V. Tishunin and N. A. Kholevo for valuable remarks and recommendations made during the examination and evaluation of the manuscript.

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INTRODUCTION

§ 1. Principal Regions and Conditions of Application of Explosive Substances

In the development of human society, the physical labor of man to a larger degree is replaced by the work of machines. Machine not only facilitates the labor of man, but also expands his ability. With the help of machines it is possible to move faster, to cultivate more land, tc transport large weights, to process the hardest materials, etc.

Machine however is not always the most effective labor replacement to man. In mining of minerals the labor of digging and other mountain and building works, and also at war is accomplished with the help of explosion.

Explosion constitutes the extremely fast release of potential energy contained in E.S. As a result of the great speed of energy release, extraordinarily high power is developed during the explosion. To obtain such power with the help of usual machines would necessitate the use of bulky and expensive mechanisms, whose use in many conditions would be practically impossible.

Explosive substances (ES) are means of work fulfillment which enables us to obtain high power at minimum of its weight and volume. This property of ES determines the expedient conditions of its application in military affairs and national economy.

In military affairs ES, which load ammunitions of different types, are the main means of manpower defeat, destruction of combat technology and military industry of the enemy. Gases are formed during the explosion of ES ammunition charge and are under pressures, destroying all that is in contact with the charge. Furthermore, gases create in surrounding air (or other medium) a shock wave, which on encountering in its path any obstacle, generates through it a strong blow. Air involved in the wave motion, completes the destruction started by the blow. The so-called high-explosive ammunitions are based on this effect.

In ammunition of fragmentation effect, explosion splits metallic body and translates high speed to its fragments, which on scattering strike the target.

In military targets ES are used in missile shells of nuclear and trunk artillery, air bombers, mortar and antitank mines, in naval barrier mines, torpedoes and depth charges.

For ES charge to produce a combat effect, it should be delivered to the target, buried on the way of combat machine movement and enemy manpower. In most cases it is necessary to move ES. The place of action, i.e., to the target. In this essentially consists the problem of basic forms of arming artillery of all types, air bombing, submarines, tanks, etc.

Transfer of ES to the place of their action is sometimes achieved only with the help of moving combat machines (aircraft, submarine, torpedoes, and others).

However, the most wide-spread means of ES transfer to the target are explosives of special kind – solid fuel. Nuclear missile or artillery trunk cannons are solid fuel propellant engines for transfer of ES warhead to the target.

Solid fuel propellant engines can develop very high power. This is necessary, in order to give the missile high speed which is required for its transfer on long distances or for the destruction of fast-moving targets. The solid propellant engine is more compact and lighter than engines of other fuel types of equal power. This promotes its wide application.

For combustion of solid fuels, air feed is not required and therefore it can burn at a greater rate in closed space. Furthermore, burning time of solid fuel may be regulated in sufficiently wide limits. In spite of relatively small combustion energy and high costs, these properties make the contemporary solid fuels, the principal type of fuel in firing nuclear and trunk type weapons.

The main consumer of ES in the national economy is the mining industry. Explosives are used in opening of deposits, passages of preparatory production and reak away of minerals in mines, pits and on open-cuts.

At present, only very soft rocks, for example sand or clay, are obtained with the help of excavators, scrapers and other machines, and without the use of ES. Also it is possible to separate from the layer with the help of pneumatic hammer, excavator, combine, cutting machine, etc., comparatively weak rocks, for instance certain forms of coal, without resorting to ES. Mining of stronger rocks requires, in addition to machines, the application of stronger forces, that are obtainable with the help of ES. On the average more than 100 g of explosives are expended for every ton of coal obtained.

If one is to consider the large proportions of coal production, then it is possible to calculate that the coal industry in the whole world consumes annually hundred thousand tons of ES. In particular, the United States alone in 1950 expended 150,000 tons of explosives for the coal production. Relatively, still larger quantities of ES are required for mining of harder rocks: different metallic ores, building stone, and also minerals used as a raw material for the chemical industry, etc.

Application of explosive methods in mountain works sharply decreases the burden and significantly accelerates the work.

Effectiveness of ES may be shown by the following example. On an area in front of the Winter Palace an Alexandrov's column was built in Petersburg. The cutting of this column from a stone chunk had to be executed with great caution in order not to split it; therefore, the work was conducted manually. For two years 600 men were occupied with this task. The volume of the unfinished column consisted of 700 m^3; 228 man-days were expended on every cubic meter of rock. By the contemporary methods of detonation on 1 m^3 of finished rock the labor expenditure may be lowered to 0.008 man-day.

Methods of conducting blastings are numerous. The simplest of which, is namely the method of imbedding the charges, where the ES are placed on the body surface which is to be destroyed, for instance; boulder, great chunk of rock, etc. Such method is simple and is carried out rapidly, but requires large expenditure of ES. Approximately 10-15 times larger than other methods, where the charge is placed inside the object to be destroyed. This deficiency is preserved to a known degree and in that case the imbedded charge is covered by stemming (Fig. 0.1) — piece of damp clay or other material, in order to delay the rate of expansion of gaseous products of explosion and thus to strengthen its effect on the object of destruction.

Fig. 0.1. Splitting of a chunk of rock by imbedding a charge with stemming. 1 — explosive; 2 — ignition cord; 3 — stemming; 4 — capsule detonator.

Fig. 0.2. Blast hole with charge of explosive. 1 — ammunition of explosive; 2 — capsule detonator; 3 — stemming; 4 — ignition cord.

Widely spread detonating method is the one where the object of destruction has a hole, usually of cylindrical form. After the inclusion of ES charge, the hole is filled with stemming, which blocks the exit of explosion gases (Fig. 0.2). In this case the explosion occurs in closed space and the destructive force is greatly increased. Holes drilled in rocks to be destroyed for placing of ES charge, depending on the dimensions are called blast holes (diameter to 50 mm, and depth to 5 m) or slit (diameter to 300 mm, depth from 5 to 50 m or more).

Blast hole method of blastings is widely used in underground preparatory works and for separating of minable ores, especially in those cases, when capacity (thickness) of its layers is insignificant. Deficiency of this method consists in large expenditure of labor and means on drilling of blast holes. In order to decrease this deficiency, the boiler charge method is used (Fig. 0.3). The bottom part of a usual blast hole is expanded in the form of a boiler by means of one or several consecutive explosions of small charges of ES. Then the formed boiler and part of the blast hole is filled by explosives; then the method of boiler charging becomes analogous to blast hole.

For destruction of mountain rocks detonation is usually carried out simultaneously or with small intervals of several blast holes resulting in better destruction of rocks. An important factor is the mutual distribution of blast holes, the distance from charges to the bared surface of rocks and the subsequent detonation.

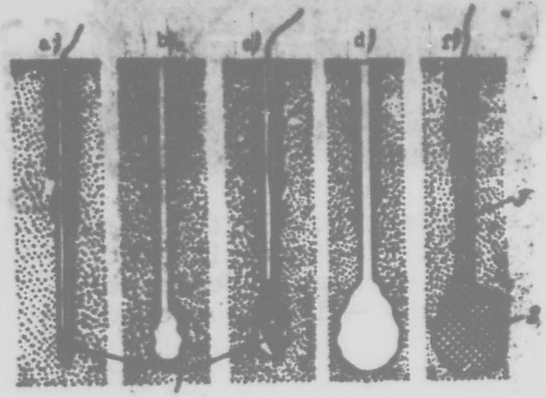

Fig. 0.3. Method of boiler charges. 1 — small charges for formation of boiler; 2 — explosive of basic charge; 3 — stemming, a, b, c, d, and e -- consecutive stages of formation and loading of boiler.

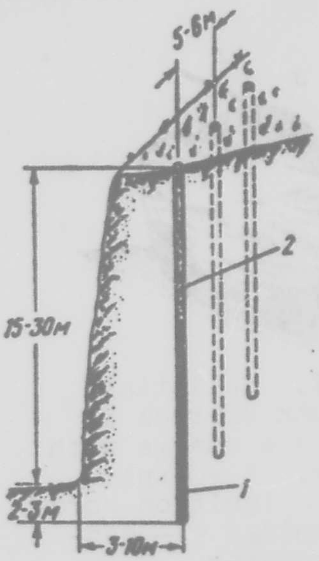

Fig. 0.4. Diagram of open-cut blasting by the slit method. 1 — explosive; 2 — stemming.

The most wide-spread method for mining of ores and other minerals on the surface, as well as underground is the method of mass cave-in caused by explosions of ES charges distributed in slits. Fig. 0.4 shows a diagram of open-cut blastings by this method. Parallel to the edge of worked rock bench a number of vertical slits were drilled with depths somewhat larger than the height of the bench. Slits are charged with solid or discontinuous charges of ES whose magnitude attains hundreds of kilograms. The charge is detonated simultaneously or in predetermined intervals. This method is distinguished by its large productivity, and the accurate calculation of the charged magnitude and its distribution corresponding to the rock. Strength is ensured by the necessary degree of splitting which is convenient for loading by excavators and further processing.

In certain forms of blastings large charges of ES in weight of tens, hundred, and sometimes thousand tons are used.

Such charges are frequently used in the so-called mass explosive ejection for obtaining ditches. By this method ditches made in mountain passes for laying roads, uncover beds of mineral deposits located near the surface for subsequent, which are subsequently mined by open method, passages are laid, rivers are blocked, and artificial reservoirs are made.

At one of the largest explosions in Ural near Korniko on 16 June 1936 conducted by engineers Paporotskiy and Selevtsev, 1800 t of explosives was detonated simultaneously. Explosion was to dislodge rocks located above a rich layer of brown coal imbedded to depths of 20 m. Thirty six charges were placed 13-18 m in depth and at a distance of 30 m from each other. The explosion of all charges was conducted instantenously. After the knife switch of the explosive network was shorted, an earth wall with a frontal width of 900 m was lifted into the air. After the explosion explosive gases escaped with a huge force, carrying with it crushed ground. Gas cloud and dust formed 3 to 4 sec after the explosion covered an area of 2 km^2 and followed the wind. The clouds attained a height near 400 m; the height of the ejected ground reached to 625 m. The explosion formed a trench of 900 m length, 85 m width, and 20 m depth, and along with it a ground of 800,000 m^3 was thrown-out. Destructive effect of the blast wave formed was comparatively insignificant despite the large magnitude of charge. Brick and wooden structures, located at distances of 350-400 m, were not damaged. Scattering of ground did not exceed 450 m. Soil oscillations were registered by seismic stations at Sverdlovsk, Moscow, and Pulkov.

Large explosions for uncovering of mineral deposits were conducted also in 1952 on territory of USSR and in 1956 on territory of Chinese People's Republic.

In the first case 1200 t of ES was detonated and the largest weight of an individual charge was 600 t, and the line of least resistance constituted 42 m. The execution of this explosion allowed the introduction in pit exploitation by a period of 3 years earlier than the foreseen usual method of development. On the basis of results obtained from the experiment, an explosion of still larger scales was conducted on the same pit in the following years. Expenditure of ES constituted 1814 t, and the biggest weight of the charge in one chamber was 1640 t.

In the Chinese People's Republic in the explosion of ores, prepared and conducted jointly by the Soviet and Chinese specialists, 9 million m^3 of rocks was destroyed, of which the useful ore constituted 2.3 million m^3. For execution of this work 15.5 thousand tons of ES detonated in 10 series was expended with the biggest quantity of ES detonated in a single series, constituted 4800 t.

In mass explosions sometimes it is expedient to mine the ore chiefly in one of either sides. In such cases directed explosions are applied.

In this method two rows of charges are filled. One row consists of weaker charges; it is detonated for the purpose of pulverizing and lifting part of the ground into air. After 1-3 sec the second row, which consists of stronger charges is detonated. The ground lifted into air by the explosion of the first row, is affected by this explosion in such a manner by which it can be moved to the desired side and away from the place of location of the second row of charges. The directing action of the explosion here promotes also that circumstance in which the second row of charges explodes in the presence of additionally uncovered surface, formed by the explosion of the first row of charges.

Mass explosions for blocking of river channels is used, mainly in the construction of temporary crosspieces, for instance, as in the construction of dams, but sometimes for other purposes.

Thus, the mass explosion prevented the destruction which would have resulted from unusually stormy seasonal floods on the river Angren in Uzbekistan in 1948. In the spring powerful flow of water gushed into adjacent irrigation ditches and ravines, overfilling them and evoking the destruction of river banks. The flood in one of the ravine of 25 m depth collapsed the banks of the irrigation ditch and covered its channel. Water, overflowing through the irrigation ditch bank got into the ravine, with the lower part blocked by a protective dam. A great reservoir formed at the dam and its level swiftly grew. Measures to raise the dam turned out to be insufficient, and 12 million m^3 of water accumulated quickly. Its breakthrough would have lead to flooding of many villages and extensive sowings of valuable cultures. The catastrophe was prevented with the help of explosion. For this reason a place was selected for higher dams with downstreams favorable for creation of crosspiece – a steep hill instead of channel bend. In this shore 12 charges of ES were deposited totaling 50 t. Explosion of these charges covered the channel of irrigation ditch, water from the river ceased to flow into it and threat of flood was prevented.

Numerous lakes were created by explosive method in regions of virgin land cultivations.

In order to dig out the foundations of one steppe lake over 100 m length, 30 m width and 15-20 m depth, only three days were needed where all the work was executed by one demolition expert and with the help of a small group of assistants. Nearly two railroad cars of explosives which were placed in nine chambers, with 6.5-7 m depth were used in the explosions. Actual chambers were prepared by consecutive explosions of small charges, which accelerated the work and made it less expensive.

Explosives in the national economy are used not only for cleaving, pulverizing and ejection of rocks, but also for many other tasks. By explosive method roads are layed through swamps, on which soft (liquid) ground does not sustain heavy excavating machines.

Work is started by loosening the upper vegetable cover of swamps by explosions. Then on loosened lay out of the road dense ground is packed forming the embankment. Under its own weight the embankment is lowered slowly into the swamp, but does not reach the bottom. At a definite depth of embankment submersion, small charges of explosive are detonated under it. Explosion displaces the semiliquid mass of earth from under the embankment, and lowers it onto the dense bottom of the swamp. Then the embankment is expanded and additional charges are detonated on each side of the embankment (Fig. 0.5). By these explosions semiliquid mass of earth is displaced a second time on both sides of the road bed, whose base takes wider and stabler form.

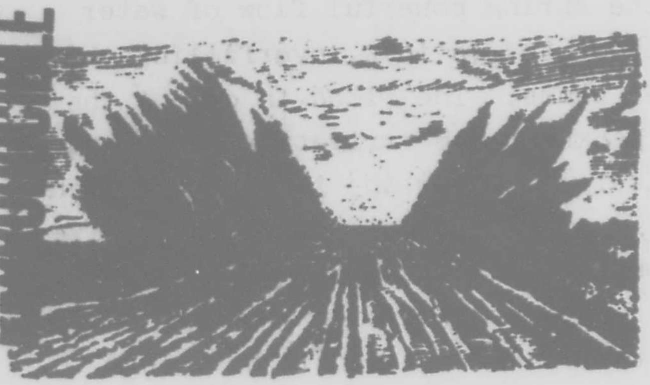

Fig. 0.5. Laying of roads through swamp by the explosive method.

In peat industry application of explosives presents a significant possibility to increase the output of this fuel.

Peat massif may be washed by hydraulic excavators only after thawing, which takes place slowly (2 to 2.5 months), therefore the spring-period which is the best period for production is not used in full measure.

With the help of explosives, frozen peat splits into pieces, which thaw after 2-3 days.

In petroleum industry ES are used for cleaning of planting pipes, torpedoing of slits, for elimination of accidents in slits, etc.

After drilling of oil wells steel pipes are lowered into it and are then cemented. In order for oil to proceed from the layer into the slit, it is necessary to pierce a number of holes in the pipe and in the surrounding cement ring. These holes are obtained by means of explosion of small cumulative charges of ES and also by shooting bullets or shells from special firing cannons, called perforators.

Explosions of charges of ES in slits (torpedoing) form a system of cracks in the rocks, which connect the layer with slit body. This increases the flow of oil or gas from the layer.

Explosives are also used in searching for new oil deposits and other minerals by the seismic survey method.

Charges of ES are placed in slit at small depths. Detonation of these charges spread waves in earth that are similar to the ones that appear during earthquakes. Waves are reflected from the layers of different rock formations which are encountered in its path. Reflected waves return to the surface of the earth and are recorded by sensitive instruments. From these recordings it is possible to determine the structure of rock layers at large depths and enables the location of oil deposits faster.

In metallurgical industry resort to explosives is made in those cases, when blast furnaces develop during the normal operation "goats" (pile) — chunk of thickened metal.

In this case a hole is drilled in the still hot metal, where small charges of explosives are placed and detonated one after another. Charges of such magnitudes of explosive force are taken which are sufficient only to cleave pieces of metal and would not damage the furnace.

In the reconstruction of cities stone structures, intended for destruction are rapidly and safely removed by explosive method. In this case correct calculation of weights and proper distribution of charges of ES exclude damages of neighboring buildings and fragments scattering with momentum does not occur.

Relatively recently ES were applied in industry for riveting by explosive method. This method has a significant value in aviation industry where it is necessary to make large quantity of rivets in the manufacture of aviation constructions.

In this method a small charge of special ES is placed in the small channel, drilled in the rivet rod. After the rivet is inserted in place, in the riveted sheets, a heated metallic rod is applied to its head. The rod heats the rivet and detonation of charge is stimulated. In the explosion the rivet end is expanded and binds the detail strongly (Fig. 0.6).

Fig. 0.6. Riveting by explosive method. 1 — explosive; 2 — heater.

Blasting applied in agriculture.

It is well known how heavy and time consuming work is presented by stubbing of stumps. In explosive stubbing of stump a hole is drilled in such a manner so that its end is under stump (Fig. 0.7). Then a charge of explosive is placed in the hole which on explosion excavates the stump from the earth and splits it.

Fig. 0.7. Stubbing of stumps by explosive method. 1 — ignition cord; 2 — stemming; 3 — explosive.

With the help of explosives soil for gardens and vineyards is loosened. Trees, planted in pits obtained by explosive method, grow faster, since the explosion loosens the soil well and, furthermore, certain products of explosion play the role of a fertilizer.

By explosive method it is possible to dig faster ditches for irrigation of fields and for draining of swamps. It is possible to dry swamps also by means of explosion piercing of watertight layer, which delays the drainage of ground waters.

The importance of ES is not lessened when applied in the struggle with forest fires. Explosions tumble trees, in order to establish a clearing for blocking the fire path.

In explosive method, the blockings of ice and wood is removed in the wood flow and accelerates the ice drifts which were blocked in the upper reaches of rivers.

With the help of ES river channels are cleared also from stones hindering the flow.

Explosives are used in the Arctic for surmounting of ice fields, which block the vessel passage, for splitting of large ice in the compression of ships lost in ice. In the last case small ice layer formed around the body of the ship by explosions, decreases the ice pressure and distributes it more evenly along the body, decreasing the danger of ship crushing.

On the whole the role of ES in mountain tasks and in certain other branches of national economy is so great, that it is difficult to imagine, as to how could the contemporary level of material culture be attained without their use.

§2. Energy and Explosion Capacity

Destructive effect of ES as was shown, may be very large, and determines the expediency and even necessity of their application in a number of cases. Arises a natural question: On what then is the destructive effect stipulated?

Frequently it is necessary to come across the opinion that basic cause of destroying action of an explosion is the huge reserve of energy, which supposedly is contained in explosives. However simple calculation shows that such an explanation is basically erroneous.

In Table 0.1 are given energy content, given out during the combustion of different types of fuels and during the explosion of different ES.

In comparing the data, given in this table, we see that in the explosion of 1 kg of nitroglycerine the energy given out is five times larger, but in the explosion 1 kg trotyl, the energy is eight times less than that from the combustion of 1 kg of coal.

Table 0.1

Substance	Heat of combustion; 1 kg kilocalorie	Heat of explosion; 1 kg·kilocalorie
Fuel		
Wood	4,500	—
Anthracite	8,000	—
Benzine	10,000	—
Explosives		
Smoke powder	—	700
Trotyl	—	1000
Nitroglycerine	—	1500

However, with such comparison we are somewhat unjust with respect to ES. The heat of combustion for 1 kg of fuel, is taken without the consideration of oxygen quantity, which is necessary for the combustion. Explosive substance does not require for its explosion additional oxygen, since it is contained in the ES. Therefore, it is more correct for the heat of fuel combustion to be based on the calculation of 1 kg of the mixture, with the necessary quantity of oxygen combustion. Such a comparison is given in Table 0.2.

Table 0.2

Substance	Thermal combustion in kilocalorie on 1 kg mixture of fuel with oxygen	Thermal explosion in kilocalorie on 1 kg
Fuel		
Wood	1900	—
Anthracite	2200	—
Benzine	2300	—
Explosives		
Smoke powder	—	700
Trotyl	—	1000
Nitroglycerine	—	1500

Although the difference in magnitudes of thermal combustion of fuels and explosion of ES in this table is less, however, even with such comparison of energy quantity given off in fuels larger than for ES.

Consequently, the huge destructive effect of explosion cannot be attributed exclusively to large energy. The actual cause is attributed to energy given off extremely rapidly during the explosion. If 1 kg of benzine burns for 5 to 6 minutes in an automobile engine then the explosion of 1 kg of the ES occurs during 1 to 2 hundred thousands fractions of a second. Energy during the explosion is given off at tens of million times faster than during burning. Furthermore, in the case of liquid and solid ES, energy is concentrated in a minute volume. Comparison between the heat of combustion of 1 l mixture of fuel with the essential quantity of gaseous oxygen and the heat of explosion of 1 l of ES is given in Table 0.3.

Table 0.3

Substance	Heat of combustion in kilocalories of 1 l of mixture of fuel with oxygen	Heat of explosion in kilocalories for 1 l
Fuel		
Wood	4.7	—
Anthracite	4.3	—
Benzine	4.2	—
Explosives		
Smoke powder	—	630
Trotyl (pressed)	—	1550
Nitroglycerine	—	2400

Assuming that all energy given off during explosion is converted into work and that the time of completion of this work is equal to the time lapsed during the explosion of ES, then it is easy to calculate what power may be attained in the explosion of ordinary ammonite cartridges applied daily in mines by tens of thousands. Diameter of the cartridge is 30 mm., length is 25 cm, and the weight 200 g. If one were to excite the explosion from the face of the cartridge, then it will propagate with the speed about 5000 m/sec and the duration of the explosion will constitute $\frac{0.25}{5000} = 5\cdot10^{-5}$ sec.

An explosion of 1 kg ammonite yields 1000 kilocalories; 200 g ammonite give 200 kilocalories, or in units of mechanical work $200\cdot427 = 85{,}400$ kg-m. Dividing the work by time and by 75, power equal to $\frac{85{,}400}{5\cdot10^{-5}\cdot75} = 23{,}000{,}000$ horse power (hp) is obtained.

Assumptions made in this calculations are not fully exact. Time of completion for the destructive work is larger than the process of explosion, but efficiency coefficient is significantly less than unity. If we will assume that because of these reasons the actual explosion power will be less by 15 times, even then it will constitute 1.5 million hp which is greater in power than the largest American hydro-electric power station Boulder Dam.

It is known that the use of explosive energy cannot replace the work of electric power stations and other power plants. Huge power of the explosion is supplied, as we saw, initially by the energy release in short time; the actual energy is not excessively great by any means.

It follows from this that the use of explosives is expedient only in those cases, when it is necessary to use very brief explosions with exceeding great power. For obtaining such effects during prolonged time period, huge quantities of ES would be needed. Thus, in order to obtain the explosive power of ammonite cartridge during three twenty-four hour days, it would be necessary to detonate about 1 million t of explosives, which is larger than all annual consumption of explosives in the mountain mining in the whole world.

Thus, ES do not replace other sources of energy; they permit only to concentrate energy with respect to time and space, to such a degree which is unattainable by other means. No machine is able, at equal weight and dimensions, to give such colossal power, as is given by explosives, and where this power is necessary, explosives are the only and irreplaceable means (if one were not to consider atomic explosion) of obtaining it.

High power is characteristic for explosives and also in cases of their application as means of throwing in the form of powders.

Let us consider as an example the shot from heavy cannon, whose shell weighs 917 kg and has an initial speed of 523 m/sec. Shell energy at the departure from the barrel constitutes 12,770,000 kg-m. This energy is attained by the shell in about 0.01 sec. Hence, the shot power will constitute 12,770,000:0.01 = 1,277,000,000 kg-m/sec, or about 17 million hp.

High power in artillery cannon is combined with large efficiency coefficient; portion of energy of powder gases, transforming into the energy of motion of the shell, attains 35% which is much larger than in steam machine, and is the same as in internal combustion engine.

However, the yield of such huge powers is conjugated with fast motor wear and is very costly. Calculation shows that the value of the work obtained with the help of instruments is many times higher than work obtained with the help of steam engine or internal-combustion engine.

Therefore, use of ES for throwing, just as for explosion, is expedient only in those cases, when it is necessary to obtain huge power, although at the expense of high cost of energy.

§3. Basic Problems of Theory of Explosive Substances

In view of relatively high cost of explosion energy it is important, particularly in wide industrial application of ES, that this energy is used most effectively. This problem is not simple. Regions of ES application, as we have seen, are extraordinarily various. Correspondingly the explosive properties of ES have to be various. For piercing of armor, for undermining of hard rocks, ES possessing maxmum sharpness of action are necessary. Conversely, for work on ejection of soft ground such sharp action is unnecessary and is even harmful.

Number of chemical compounds applied as ES or entering into composition of different explosive mixtures, is small. Therefore, it is necessary to know how to prepare ES from few components, having very wide range of explosive properties, responding to different requirements of explosive technology. For that it is necessary to know, how is the explosive action of ES dependent on composition, on energetic, physicochemical, and physicomechanical properties of components and their mixtures, in particular, on the degree of crushing each of the components, on the character of their mixing, on density of powdery ES, forms and dimensions of charge, etc.

Large significance has the possibility of control by explosion, in particular, the possibility of concentrating or, conversely, dispersing of its action. In the first case it may be essentially an intensive breakthrough, cracking action of explosion; in the second — unnecessary splitting of undermined material is prevented. This requires knowledge of regularities of explosion flow and its mechanical action on different conditions.

Essential, and sometimes decisive role, for possibility of application of ES, plays its sensitivity. ES can possess the best indexes of explosive action, but if it explodes from a light blow, weak friction or small heating, then such a compound cannot find technical application.

Of large practical value is the question of stability of ES during storage. As a rule, explosives are used on the day of manufacture, but after a lapse of more or less prolonged periods, in certain cases measured by many years. Therefore ES should be able to sustain prolonged storage without essential changes of its properties.

One of the basic characteristics of ES, determining its stability, is the speed and the character of slow chemical transformation, to which all ES are subject to larger of smaller degree. Speed of this transformation depends to a greater degree on temperature of the substance; on heating ES it is accelerated and can lead to possible ignition and burning.

Burning of ES has an independent interest, since the use of ES (powders) is for purposes of throwing.

Furthermore, at certain determined conditions burning changes into explosions. In order to exclude the possibility of such transition during powder burning in fire arms, it is necessary to know and regulate the stability of burning, and for prevention of destructive explosions of ES in factories and storage houses, furthermore, it is necessary to prevent possibility for burning to start.

The tremendous consequences resulting from insufficient mastery of conditions which lead to excited explosion is exemplified by the grandiose catastrophe, which happened in Germany in 1921.

At the factory in Oppau, pourable potassium nitrate fertilizer mixture containing approximately 50% of ammonium nitrate and 50% of ammonium sulfate was produced. As a product of seasonal consumption it was stored in large quantities in the factory storage house and during the time of prolonged storage it was compressed into stone-like mass. Splitting of this mass by mechanical means turned out to be difficult task and it was decided to resort to explosive method. For clarifying the ability of pourable-potassium nitrate to be subjected to explosions the preliminary experiments conducted gave negative results. After this the loosening by explosion was conducted at considerable length of time – in total about 20,000 blasts were conducted without any mishaps – until finally, on the morning of 21 September 1921, the storage house of pourable-potassium nitrate together with factory were lifted into the air. In place of the factory a crater of 165 m length, 96 m width, and 18.5 m depth was formed (Fig. 0.8). In the explosion over 500 people were killed and 2000 people were seriously injured.

The basic cause for the explosion, the largest in history of chemical industry, was attributed to incorrect evaluation of the explosion sensitivity of pourable-potassium nitrate.

Fig. 0.8. After explosion in Oppau.

The most important problem of safety engineering in the application of ES in coal mines is the prevention of methane-air and dust-air mixtures from exploding in blastings. One of the basic ways, of ensuring the solution of this problem, is the application of so-called special safety ES, possessing relatively low ability to ignite methane-air and dust-air mixtures.

Thus, for effective, and safe manufacture and application of ES it is necessary to know:

1. Relation between the composition of ES, its physicochemical, physicomechanical properties and form of the charge, on one hand, and its explosive effective — on the other.
2. Regularities of mechanical effect of explosion on the environment.
3. Conditions and mechanism of bringing about of burning and explosion at different effects on ES.
4. Stability of ES during storage.
5. Mechanism and principal characteristics of three basic conditions of transformation of ES: slow chemical transformation, combustion and explosion.
6. Conditions of ignition of explosive gas-air and dust-air mixtures during blastings.

Study of these questions constitutes the subject on the theory of explosives.

CHAPTER I

GENERAL CHARACTERISTIC OF EXPLOSIVE SUBSTANCES

§ 1. Explosion Phenomenon

Various forms of explosions exist and correspondingly are different determinations of "explosion" understanding.

In the widest meaning of the word, explosion is applied to the physical or chemical transformation of a substance, which is accompanied by extremely rapid transition of its energy into energy of compression and motion of the parent substance or the products of its transformation and the surrounding media.

Phenomenon of explosion in principle includes two stages: 1) stage of energy transformation of one or another form into energy of highly compressed substance and 2) stage of expansion of the compressed substance. In the expansion process the potential energy of compression usually changes into mechanical work. This work leads the surrounding media into motion, which may cause its destruction, if the acquired pressure exceed compression strength.

Thus, the extremely fast appearance or, more accurately, the development of a pressure effect which is, as a rule, quite large, constitutes the basic characteristic criterion of explosion. As a result of the rapid development of the pressure and its great magnitude, it is this exceptional power, which is peculiar to explosion.

Several different types of initial energy of explosion are possible: electrical, kinetic, thermal, energy of elastic compression, atomic, and chemical.

Thus, explosion can occur during strong spark discharge, for instance under water, or during transmission of powerful current through thin wire; besides, electrical energy changes into energy of heated and compressed air or vapors of water or metal.

In the impact of a body moving with great speed against a durable barrier its kinetic energy changes into thermal; strongly compressed gases, may be formed at sufficient magnitude of energy. Explosions of such nature occur during the fall of big meteorites.

Cases of explosion of bottles with compressed gases are known, which developed due to excessive increase of pressure, for instance, from accidental heating up, or due to decrease in durability of wall as a result of corrosion, mechanical damages and etc. These explosions occur at the expense of thermal energy of compressed gases. To the same type pertain explosions of boilers, accompanied by fast transformation of overheated water into steam. In overheating of water in boiler, the vapor pressure increases to a magnitude, exceeding the resistance of walls of the boiler. After the burst of boiler, the steam contained in it and also steam, from overheated water rapidly expands due to drop of pressure and produces work of destruction.

Examples of explosion resulting at the expense of energy of elastic compression, are majority of earthquakes. Pressures developed in separate sections of Earth's crust can embrace very large volumes;

they are stored, and then during earthquake huge quantity of energy are suddenly liberated. Energy of the strongest earthquake is estimated at 10^{23}-10^{25} erg, i.e., exceeds the energy of explosion of million tons of usual explosives.

It is possible to reproduce explosions of similar type at small scales. Thus, an explosion can occur if one were to freeze water in durable steel bomb, filled to the top. Due to the expansion of water during its transformation into ice, the pressure in the bomb increases and is able, in the end, to exceed the resistance of walls, as a result of which a burst of the bomb will occur. Potential elastic energy of compressed water changes into mechanical work of destruction of the bomb.

Curious case of this type of explosion occured on one of the railroad stations in Eastern Siberia, where it was desired to store ice for the summer, by freezing water in the winter in a huge box with capacity of more than thousand cubic meters. This resulted in the explosion of the box with terrific noise; huge chunks of ice flew more than 20 m into the air.

Still stronger was the explosion of frozen mound on river Onon in Eastern Siberia. Mound exploded, scattering huge chunks of ice and ground, the largest of which had the dimensions of 19 × 5 × 2 m, and total weight of five thrown-out chunks reduced 453 t. During the explosion, huge quantity of water escaped from the mound, carrying certain block mass to 120 m; in addition a small bridge on the road was destroyed.

In both these cases the role of a shell played ice casing, surrounding the liquid nucleus.

Atomic explosion occurs as a result of chain reaction of fast division of certain heavy atomic nuclei, during which intranuclear energy is converted into kinetic energy of nucleus fragaments. During thermonuclear explosion, energy separates at the expense of light elements forced from atomic nuclei, in particular, deuterium and tritium, nuclei of large mass elements. Since the energy, which separates during the atomic and thermonuclear explosions per unit of mass substance, is several orders larger than from chemical reactions, then the force of explosion is correspondingly incomparably larger.

At last, an explosion can occur at the expense of potential chemical energy, which is converted into energy of compressed gases as a result of fast flow of chemical reaction.

In the epoch of pre-atomic power engineering, this type of explosion had predominant value during the use of explosion phenomenon in industry, as well as in military affair and preserves basically this value up to the present.

At this time main attention will be given to this type of explosion (explosion of explosive), to which it is possible to give the following parameters:

Explosion of ES is called a fast chemical transformation, proceeding with the yield of large quantity of heat and formation of gases.

Explosion of ES can time place in two different forms: 1) homogeneous and 2) self-propagating transformation.

Homogeneous explosion. Let us gradually heat a vessel, filled with explosives. In conformity with increase of temperature of ES the rate of its transformation reaction will also increase. Since transformation proceeds with liberation of heat, then the temperature of ES will be increased not only due to external heating, but also due to the heat of reaction. This self-heating under known conditions becomes self-accelerated that in turn leads to sharp acceleration of reaction, as a result of which ES are converted rapidly into strongly compressed gases.

This – homogeneous chemical explosion, does not have practical application in explosive technology.

By principle of its own development, homogeneous chemical explosion is similar to atomic explosion, which is based on nuclear fission. In case of ES development of chemical reaction is stimulated by separation of heat; in case of atomic explosion nuclear reaction occurs development of which is stimulated by the generation of neutrons.

Self-propagating explosion. Formation and development of chemical explosion is possible in other form. By assuming that in a small part of the charge of ES by means of strong heating a rapid chemical reaction is initiated. At known conditions this reaction will spread spontaneously with great speed from its excitation point to the boundaries of charge. On the use of this self-propagating – explosion all contemporary explosive technology is based on.

Ability of chemical reaction in certain conditions to have unlimited self-propagation is the essential peculiarity of given form of explosion. In accordance with the above it is possible to give the following parameters to this form of explosion of ES.

Explosion of ES is called self-propagating, with great speed of chemical transformation, if it proceeds with the yield of large quantity of heat and formation of gases.

Due to the rate, with which the reaction proceeds in ES, the forming gases, even in the absence of durable shell, have high pressure and produce strong impact on the surrounding media, destroying and scattering it, and also provoking shock waves in it.

§ 2. Basic Conditions for Reaction Taking Place in the Form of Explosion

From determinations, given at the end of § 1, four basic conditions are divided, which a chemical reaction should satisfy so that it could proceed in the form of explosions:

1) exothermic nature;

2) formation of gases;

3) high speed;

4) ability to self-propagation.

All these conditions are not absolute and independent from each other. Thus, high rate of reaction is determined not only by the magnitude of rate constants, but also by temperature, attained during the reaction, in other words, thermal effect of latter. In exactly the same way the ability of reaction to self-propagation, depends to a greater degree on the rate of its flow and thermal effect. Absence or presence of gases in the reaction products also to a known degree is caused by the thermal effect. Finally, the thermal effect itself, can change, depending on the conditions of reaction procedure in particular, pressure and temperature.

Four conditions in its own combination determine not only the possibility of self-propagation of chemical reaction in the form of explosion, but also the mechanical action of the latter. Let us consider their value in each relation.

1. Exothermic Nature, Speed and Formation of Gases as Factors, Determining Possibility of Explosive Propagation of Chemical Transformation

Exothermic nature of transformation of ES. Exothermic nature of transformation of ES in products of explosion can have various causes. Thus, if chemical compound is endothermic, i.e., it was formed from elements with absorption of heat, then during the reversible process – disintegration of compounds into elements – the corresponding quantity of heat is given off. Nitrogen Trichloride can serve as an example, it decomposes with explosion by reaction

$$NCl_3 \rightarrow \frac{1}{2}N_2 + 1\frac{1}{2}Cl_2 + 56 \text{ k/cal}$$

On the other hand, atoms, contained in molecules of ES, can form with liberation of heat other compounds. This takes place, for instance, during the explosion of nitroglycerine, whose heat of formation from the elements is positive, but much less than total heat of formation of those compounds (H_2O, CO_2), which are formed during explosion. Well known ES (for instance, fulminate of mercury hexogen, tetryl), whose thermal effect of explosion is determined simultaneously by their endothermic property and formation during the explosion of strongly exothermic compounds.

Exothermic nature of transformation is determined by the fact that bond strength between atoms in products of transformation is significantly larger than in the ES. Hence, it is clear that ability to have an exothermic reaction depends on chemical structure of substance.

First attempts of data systematization on this dependency were made by Bayer and Van't Hoff.

Bayer arrived at conclusion that endothermic property, determined by the explosive ability and also the high sensitivity of acetylene and polyacetylenic compounds are related to the significant internal stress at the triple carbon bonds, in which the angles between valence bonds experience the biggest deviation from the normal value of 109.5°.

According to Van't Hoff, chemical inertness of carbon bond makes possible the existence of thermodynamically unstable compounds, whose formation from elements is related to the significant expenditure of energy; therefore, these compounds are able to disintegrate with liberation of heat.

Of still greater importance, is the possibility of formation from elements of strongly exothermic compounds entering into composition of ES. Ability to have an exothermic reaction is according to Van't Hoff the main condition of explosiveness.

Endothermic compounds can be obtained at various combinations of atoms of elements in molecule. In particular, certain compounds, are endothermic where atoms of the same elements are bonded to each other. These are, for instance, compounds containing -O-O- grouping like ozone or hydrogen peroxide. Another example can be compounds, containing -N=N- grouping. A third example is the -C≡C- grouping in acetylen and its derivatives.

With absorption of energy certain compounds are formed also, which include atoms of different elements, such as nitrogen and oxygen (for instance, NO, N_2O), chlorine and oxygen (for instance, ClO_2).

Relatively small bond strength in N-O and Cl-O is maintained in nitro compounds, nitrites and nitrates, correspondingly also in chlorates and perchlorates. Analogous properties possesses also bonds of carbon with nitrogen.

Totality of groupings, whose presence and accumulation in molecule can render explosiveness to the substance is given in Table 1.1.

Table 1.1. Atomic Groupings, Which Render Explosiveness to Compounds (According to Van't Hoff)

$O—O$ $H—Sb$ $N—Cl$ $C—S$	$N=N$ $H—As$ $N—S$ $C—N$	$C\equiv C$ $O—N$ $N—Se$ $C—Ag$	$O—Cl$

Main practical value in the contemporary explosive technology have organic substances, containing NO_2 – group, bonded to carbon directly (nitro compound), through nitrogen (nitramine) and through oxygen (nitro esters). The main part of thermal effect during explosion of such compounds is obtained at the expense of oxidation of carbon and hydrogen, containing in their molecules, oxygen of nitro group.

Considerations of Van't Hoff are correct in general, inasmuch as he underlined the value of exothermic nature, as necessary condition of explosion and indicated two possible sources of liberation of heat during chemical reaction: disintegration of endothermic and formation of exothermic compounds. However, this factor does not determine still synomymous explosiveness of substance.

Rate of reaction and its ability to self-propagation. Characteristic (although frequently insufficiently underlined) peculiarity of ES is the ability of initiated in them local chemical reaction in known conditions, to unlimited self-propagation. This self-propagation occurs as a result of propagation by thermal wave of ES, transmitted by one or other means, for instance thermal conduction, shock wave etc., and provoking chemical reaction in its passage. Thermal wave in turn is supported by chemical reaction, which it evokes.

Essential factor, determining to possibility of appearance and propagation of independent thermal wave, is its intensity, i.e., temperature, obtainable in it. This temperature is determined first of all by the thermal effect of reaction. However, also important essential factor is the chemical reaction rate of transformation of ES at a given temperature. The larger the rate constant of reaction, the less sufficient is the temperature for obtaining a definite rate of transformation in that layer of ES, through which at a given moment passes the thermal wave. Furthermore, at greater reaction rates the lesser its duration, correspondingly less thermal loss and higher temperature actually obtainable during reaction procedure. Thus, along with exothermic nature during self-propagation of reaction, a definite role plays also the stability of molecules, more accurately its reactivity, characterized in the first place by activation energy — minimum energy, which a molecule should obtain in order to react.

Besides the matter is not in the absolute value of the activation energy, but in the relationship between heat of reaction and activation energy. At small activation energy, small heat of reaction is sufficient, in order for a substance to be able to explode; however, a substance may be able to explode in that case, if the exothermic reaction of its transformation has a high energy of activation or by whatever other causes (for instance, due to heterogeneity of the system) takes place with relatively small speed. In this case it is necessary only, that to thermal effect of reaction was correspondingly larger.

Substance may be very unstable and at the same time not be explosive, if the thermal effect of the reaction is small. In exactly the same way a substance may be very stable and simultaneously able to explode, if the heat of reaction is great as compared to activation energy.

It is possible to give many examples, when substances are unstable but nonetheless is not explosive. Thus, ammonium carbonate decomposes with great speed already at 60°, mercuric oxide decomposes into elements at 100°. Both these substances are not explosive, although their stability is much less than the typical ES like trotyl or picric acid. This is explained by the fact that processes of decomposition of ammonium carbonate and oxides of mercury takes place with absorbtion of heat and therefore, cannot lead to heating up of neighboring layers of the substance and excitation of chemical reaction in them.

It is possible to imagine, an unstable substance, which decomposes on heating with evolution of certain quantity of heat, but nonetheless not able to explode under usual conditions of reaction of the latter. Such are for instance, according to I. F. Blinov, complex compounds of certain aromatic nitrodiazocompounds with zinc chloride; they have low flash temperature and give large frequency of explosions during impact, exceeding in this respect such sensitive explosive, such as "TEN." At the same time they do not detonate from capsule-detonator even in wide 40 mm diameter steel tube.

Another example is potassium chlorate whose decomposition into potassium chloride and oxygen is weakly exothermic (~10 kilocalore/mole) and proceeds under usual conditions without explosion. Well known, however, is the strong explosion of potassium chlorate during fire. It is possible to explain by the fact that large masses of chlorate were melted, and the reserve of energy increases to a such degree that explosion is possible.

Thus, explosiveness may be attained at the expense of large exothermic nature of the reaction, and also at the expense of low stability of molecule. Usually a rush is made to use the first factor as far possibly because the magnitude of thermal effect of the reaction determines the action of explosion, and also because low stability of molecule usually leads to low chemical stability and to high sensitivity of ES, which increases the danger of its production and application.

In accordance with the above contemporary ES in majority are comparatively stable compounds; they ignite and explode relatively with difficulty. For illustration, it is reminded, that picric acid was applied as a paint during 100 years, before it was clarified that it was a strong explosive. It is much more difficult to ignite trotyl than paper, but all the more so benzine; ammonium nitrate or its mixture with trotyl is not possible to ignite with match even at low pressures and room temperature, and in small quantities in general, they do not burn.

Theoretically it is possible to imagine of ES with such large ratios of heat of reaction to activation energy, that self-propagation of explosive transformation will occur already during decomposition of only one of its molecule. However, simple calculation shows, that such substance would be completely decomposed in short time and practically could not exist.

At the same time a substance, in which decomposition of one molecule does not lead to self-propagating reaction, it may be possible that if at one place and simultaneously decomposition occurs not only in one molecule, but in significant number. In actuality, energy that is given off during decomposition is transmitted to neighboring molecules. For one molecule the number of these neighbors is great; furthermore, if the neighboring molecule, on obtaining energy, did not decompose, then it rapidly transmits it further. Significant and prolonged concentration of energy does not appear.

In case of decomposition of group of molecules, the number of neighbors for every reacting molecule is less and energy dissipation occurs slower, since the conduction of energy beyond the limits of hearth compensated by its entrance from the internal layers of hearth.

It follows from what has been said that to ability of reaction of transformation of ES to self-propagation, depends not only on thermochemical and kinetic characteristics of the substance (heat and reaction rate), but is determined also by the possibility of re-creation of high concentration of energy in layers of ES, neighboring with initial hearth of reaction.

This possibility depends, as was shown, in particular, from dimensions of initial hearth of reaction. Other factors also play role which affect the development of reaction and dispersion of energy (pressure, presence and durability of shell, physicomechanical structure of ES, etc). They will be considered in detail in § 12, Chap. IV. In particular, during cylindrical charge, self-propagation turns out to be impossible, if its diameter is less than that determined for a given ES magnitude.

Thus, actual idea of explosiveness does not have absolute character and is not qualitative, but quantitative.*

It is impossible to irrelevantly characterize a charge as explosive. It is necessary to indicate condition, at which it is explosive. If however, these conditions are not known, then this signifies only, that the substance, of which this discussion is about, is explosive under those usual conditions (dimensions of charge, density and etc), which are characteristic for its technical application.

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*We talk about substances, capable of exothermic reaction. If a substance does not possess this ability, it can then be considered incapable of explosion.

Is possible to note also, that one substance is more explosive than another, if one is able to explode under these conditions at which other compound to it are still not able.

As was indicated above, self-propagating transformation of ES cannot be initiated by decomposition of one of its molecules. What dimensions are necessary for this hearth decomposition is not established exactly. Apparently, they are very significant and are measured at many billion molecules, at least for ES or that degree of stability, which is applied in technology.* At large critical sizes of the main self-propagation reaction the probability of its spontaneous appearance during usual, low temperatures is practically equal to zero and the explosion may be initiated only sufficiently by intense external influence.

Role of external influence leads, as a rule, to creation in explosive of heating source, which starts the self-propagation reaction. Such heating source can be formed and as a result of slow thermal decomposition of ES, if this exothermic decomposition developes to a greater speed.

From the above description it is clear that the ability of a chemical reaction to have an independent propagation in the form of an explosion, is the fundamental characteristic of explosives, determined by the relationship of basic parameters in it of chemical reaction and conditions of energy dissipation.

Formation of gases. Besides energy and kinetic characteristics of the substance, possibility and especially the rate of self-propagation of the reaction depend also on conditions of energy transfer.

If all the energy separates in the form of heat, then its

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*It is known, that mechanical mixtures of such hard components, which by themselves are not explosive are capable of explosion; besides each component particle consists of huge number of molecules. This circumstance also indicates to the fact that the minimum dimensions of reactions center, leading to the development of explosion, are very large as compared to dimension of molecule.

transmission occurs only by means of relatively slow process of heat transfer; correspondingly the rate of propagation of reaction is small. This case takes place during burning of explosives. Increase of pressure in the absence of the shell will be very small, and the mechanical effect of the reaction products is insignificant.

If however, the chemical reaction takes place locally then along with the energy effect, large pressure developes, and the energy transfer in known conditions can be carried out by means of propagation of pressure jumps so-called shock wave. The rate of energy transfer in this manner is incomparably larger than the heat transfer and correspondingly the chemical reaction propagates rapidely. Increase of pressure in it is very great and equals its destructive action. This is detonation of explosives.

Necessary condition for such conditions of propagation reaction is the presence gaseous products (at corresponding temperature) among it. The formation of gases is concluded in this value as a condition as a possibility of detonational self-propagation of chemical reaction.

From the above it is clear that the same chemical transformation can take place absolutely differently with respect to the rate of its propagation and the character of external mechanical effect, depending upon the type of mechanism of energy transfer from the reaction products to the unreacting substance. The characteristics of chemical transformation reaction of ES themselves — its energy, activation energy, aggregate state of reaction products — do not condition the inevitable explosive character of transformation. This may be evident at least from the fact that ES are able not only to detonate or burn, but are also capable of slow chemical transformation.

2. Exothermic Nature, Formation of Gases the Rate of Chemical Transformation and Its Ability of Self-Propagation as Factors of Destructive Force of Explosion

Exothermic nature of reaction. Strongly compressed gases of high pressure formal during an explosion produce external work, which is accomplished at the expense of energy, given off during the reaction. Therefore, it is clear that transformation, which takes place at least yielding gases, but with expenditure of heat [for instance, decomposition of ammonium carbonate $(NH_4)_2CO_3=2NH_3+H_2O_{(gas)}+CO_2-47$ kilocalories] cannot have a character of explosion.

The value of thermal effect as a factor, determining the action of explosion, may be explained by the following example.

By taking two durable steel bombs with a capacity of 10 liters each, and the first containing 5 kg of liquid carbon dioxide, and the second — mixture of carbon (for instance, soot) with liquid oxygen. If in every bomb is introduced an electrode tonator which is then detonated, then in the first case the steel shell will remain whole, while in the second it will be torn to small pieces. In both cases after the explosion an equal quantities of the same substance is obtained carbon dioxide. Difference in action is caused only by the fact that in the second case during the formation of carbon dioxide, for every kilogram of CO_2 over 2000 kilocalories are given off. At the expense of this energy the work of shattering the bomb is performed.

Clear dependency between thermal effect of reaction and the ability of a substance to explode is revealed in the comparison of properties of oxalates of different metals. These compounds have according to Bertlo similar for decomposition, equation, formed during the metal and carbon dioxide decomposition but are distinguished by thermal effect of this reaction (Table 1.2).

Table 1.2. Heat of Decomposition and Presence of. Explosive Properties for Oxalates of Different Metals (According to Bertlo)

Substance and equation of decomposition	Thermal effect kcal/mole	Presence of explosive properties
$ZnC_2O_4 \rightarrow 2CO_2 + Zn$	−49,1	Not explosive
$PbC_2O_4 \rightarrow 2CO_2 + Pb$	−16,7	Same
$CuC_2O_4 \rightarrow 2CO_2 + Cu$	+5,9	Explosiveness is doubtful
$HgC_2O_4 \rightarrow 2CO_2 + Hg$	+17,3	Explosive
$Ag_2C_2O_4 \rightarrow 2CO_2 + 2Ag$	+29,5	•

Experiment showed that, only oxalates of mercury and silver, decomposed with significant liberation of heat, and possess explosive properties. Oxalates of zinc and lead have a negative heat of decomposition and are not able to explode.

When substance, depending upon conditions is able to be decompose into different directions, only those are accompanied by explosion, which are related with the evalution of significant amount of heat.

Thus, ammonium nitrate, in agreement with Bertlo, decomposes at different conditions according to the following equations:**

$$NH_4NO_3 \rightleftarrows HNO_3 + NH_3 - 40,8 \text{ kilocalories} \quad (1)$$

This reaction occurs at lower temperature than any other decomposition, and is endothermic.

$$NH_4NO_3 \rightarrow N_2O + 2H_2O + 10,3 \text{ kilocalories} \quad (2)$$

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*Given Bertlo equation for decomposition, have an approximate character; oxides of metals and carbon dioxide are formed also in reality.

**Thermal effects of reactions are given constant volume.

Decomposition with the formation of water and nitrous oxide proceeds at careful heating and at temperature near 200°C

$$NH_4NO_3 \rightarrow \frac{3}{4}N_2 + 2H_2O + \frac{1}{2}NO_2 + 28.1 \text{ kilocalories} \qquad (3)$$

Formation of nitrogen peroxide is observed during rapid heating of ammonium nitrate to 400-500°C, for instance, if one were to throw a crystal of ammonium nitrate in the heated red-hot test tube.

$$NH_4NO_3 \rightarrow N_2 + 2H_2O + \frac{1}{2}O_2 + 30.2 \text{ kilocalories} \qquad (4)$$

This, reaction is observed during the action of powerful initial impulse, for instance the explosion of capsule-detonator in combination with the intermediate detonator.

It is clear that, reaction (1) under any conditions cannot proceed with explosion, whereas during the decomposition according to equation (4), ammonium nitrate gives such strong explosion that it may be used for execution of blastings.

In apparent contradiction with first condition to possibility of explosion (exothermic nature of transformation) is one reaction – reaction of explosion of barium azide. If one were to consider that like other azides it is decomposed during the explosion to a metal and nitrogen, then the heat of such decomposition will constitute by thermochemical calculation – 6.32 kilocalories. At negative heats of dissociation, barium azide must not be explosive. At the same time, as was shown by corresponding experiments, barium azide possesses weak explosive properties; in particular, it gives a distinct flash on heating, and also reveals significant sensitivity to impact.

Research showed that in reality on heating only part of barium azide breaks up into elements, while the larger part of barium converts into nitride – compound with significant positive heat of formation. The total reaction may be expressed by equation

$$4BaN_6 \rightarrow Ba + Ba_3N_2 + 11N_2 + 71{,}0 \text{ kilocalories}$$

Thermal effect of this reaction is positive, and which is explained by the explosiveness of barium azide.

Formation of gases. The value of this factor for action of explosion, may be explained by the following example. Let's take two closed vessels with capacity of 2 liters each containing 1 liter of solid or liquid substances A and B. Both these substances are able to have an exothermic reaction, giving identical increase in temperature, for instance up to 2730°K. Substance A gives, under these conditions only liquid or solid products, substance B — only gases. If the air from the vessels was preliminarily pumped, out, then the case of A, products of reaction will not render noticeable pressure on the walls of the vessel, and their action will be only thermal. In the case of B, even during isothermal transition of the substance into gases a pressure about 500 a-t,* is created since the density of gas at normal conditions is approximately thousand times less than the density of the condensed substance. If one were to consider also the increase of temperature, then during the calculation, according to the law of Clapeyron, a pressure of 5000 a-t is obtained actually by pressure will be still larger by virtue of the fact that laws of ideal gases in this case are inapplicable.

Thus, formation of gases makes an explosion possible, i.e., sharp increase of pressure and transition of potential energy of explosive into mechanical work. This is determined, first, by the fact that gases have significantly smaller density then solid or liquid substances, so that the transition of solid or liquid substances

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*a-t means technical atmosphere.

into gases at constant volume strongly increase the pressure; secondly, by the fact that gases have significantly large coefficient of volume expansion than solid or liquid substances. Thanks to these two peculiarities, gases are those direct physical agent which, on expansion produces work of explosion.

Even strongly exothermic reactions which do not generate gases cannot take place with explosion. For instance, thermite reaction

$$2Al + Fe_2O_3 \rightarrow Al_2O_3 + 2Fe + 201 \text{ kilocalories}$$

in spite of large quantity of heat given off, does not produce explosion.*

Two reactions were known, to proceed with explosion, when gases, did not seem to form. Thus, silver acetylide is decomposed by equation

$$Ag_2C_2 \rightarrow 2Ag + 2C + 84 \text{ kilocalories}$$

From the equation it is seen, that gases are not formed, but nonetheless strong explosion occurs. Research established that the explosion of silver acetylide is related to the content of impurities in it silver nitrate and silver oxide, accompanying it during its usual method of preparation. During the silver acetylide decomposition these impurities are decomposed at the expense of the heat given off and form gases, which are necessary for explosion. If one were to change the method of silver acetylide synthesis in such a manner so that a purer product was obtained, then the less impurities it will contain, then the weaker will its explosiveness be expressed. Absolutely pure silver acetylide gives off deaf sound on igniting in air, which is related to the rapid heating of adjacent layers of air. In vacuum it is decomposed without any criteria of explosion.

Second reaction of similar type is expressed by equation

$$2Al + KClO_3 \rightarrow Al_2O_3 + KCl + 410 \text{ kilocalories}$$

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*If thermite contains air or impurities, which form gases, then it can cause explosion, and under known conditions even strong ones.

Mixture of 31 parts of aluminum and 69 parts of potassium chlorate responding to this relationship, during the corresponding tests, it distinctly reveals its ability to explosion. At the same time gases are lacking at the right side of the equation.

However, the moment of explosion, there are gases nevertheless since the temperature of the reaction products of this mixture is very high (by calculation more than 4000°) and potassium chloride, which boils at 1415°, can change into gaseous state.* This assumption is confirmed by the character of pressure change during the explosion in closed space (bomb Bikhelya). Usual explosives show increase of pressure with subsequent drop to certain finite value, corresponding to the pressure of gaseous explosion products at room temperature (bomb before explosion is evacuated). Mixture of aluminum and potassium chlorate gives rise in pressure in exactly the same way (indicating on formation of gases), but then the pressure drops to zero, since gases potassium chloride, by condensing, changes into the solid state, in which the tension of it, vapors is practically equal to zero. Thus, in both cases considered explosion is related with the presence of gases.

High rate of reaction. Particular high reaction rates ensures that huge power, which is characteristic criterion of explosion. Therefore, even if the first two conditions are fulfilled, but the reaction rate is small, then explosion does not occur.

Thus, carbon burns in air without any explosion. Besides large quantities of heat and gases are given off but the reaction rate is small, since it takes place only on the surface of air contact with the burning material, but this surface is small. If it is increased, for instance, its carbon is crushed and the coal dust is suspended

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*According to Apin formation of gases during explosion of studied mixtures can occur also due to the decomposition of potassium chlorate with oxygen evolution which proceeds somewhat the oxidation of aluminum.

in air state, then this suspension explodes; the force of the explosion of such a mixture is small due to its small density and correspondingly small pressure, which is obtainable on combustion.

If one were to increase the density of this mixture, and consequently its volume capacity, applying air or oxygen not in gaseous form but into liquid form an oxyliquite will be obtained — one of the strongest ES.

Change of rate at other equal conditions strongly indicates the force of explosion. Thus, nitroglycerine depending upon certain conditions can explode with different speeds: about 8000 and about 2000 m/sec. Correspondingly mechanical effect of explosion, for instance, pressing on the lead cylinders, strongly changes it (Fig. 1.1).

Ability of chemical transformation to self-propagation. In conditions of application of ES chemcial transformations excite in any small part of the charge, after which it distributes all over the charge. For instance, if explosion is evoked by ignition of ES then direct influence of flame subjects only small part of the substance. Initiated local chemical reaction in this part of the substance should be able to spread independently and rapidly all over the remaining substance. In the absence of ability of chemical transformation to such self-propagation or during its loss, the ES cannot be applied in practice.

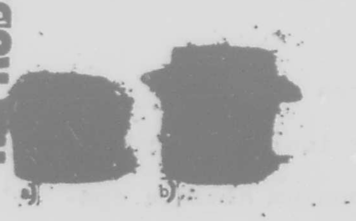

Fig. 1.1. Deformation of lead cylinder on detonation of nitroglycerine with great (a) and small (b) speed.

Thus, for instance, if the diameter of cylindrical charge of ES is greatly decreased and if one were to introduce into the substance too many inert additions, and if the ammount is packed excessively, and also if happened aging of the gelatin-dynamite occurred then ability of explosive reaction to self-propagation decreases. If this decrease is significant, then ES becomes unfit for practical application.

Thus, ability of chemical transformation to independent propagation is the most important characteristic of ES and also from the point of view of real possibility of its technical application.

§ 3. Basic Types of Explosive Substances by the Composition and Classification of Their Application

In principle, as explosive may be any mixture combustible with the oxidizer. The oldest explosive — black (smoke) powder — is a mixture of two fuels (carbon and sulfur) and oxidizer (potassium nitrate). Other types of similar mixtures — oxyliquites — are thinly dispersed fuel (soot, moss and etc.), impregnated by liquid oxygen.

The widest applied type of explosive mixtures are ammonites — mixture of ammonium nitrate with explosives (for instance, trotyl) or nonexplosive (for instance, peat) fuels. Ammonium nitrate contains excess of oxygen in the nitrate residue which is the oxidizer; simultaneously it contains combustible elements (hydrogen of the ammonium group) and is capable therefore, of an exothermic reaction, which can take place into the form of an explosion.

However, the heat of explosion of ammonium nitrate is small; simultaneously it possesses low sensitivity to detonation. If however, a fuel is added to ammonium nitrate, a fuel possessing explosive properties, then the heat of explosion and sensitivity to detonation increases. As oxidizers in explosives, besides nitrate, other salts may be used, for instance, chlorates, perchlorates and others.

In order to obtain an ES from a solid oxidizer and a fuel, they must be strongly crushed and thoroughly mixed. Chemical reaction in the beginning proceeds only on surface of the particles and takes place faster if this surface is larger. However, not matter how crushed are the solid component parts of the mixture, it is impossible to reach such uniformity of composition, at which next to every molecule of the fuel a molecule of oxidizer would be precent. Therefore, in mechanical mixtures the reaction rate during explosion does not attain the biggest value.

This deficiency is absent in explosive chemical compounds, in whose molecules enter combustible elements (carbon and hydrogen) and oxygen. It is clear that in molecule of such substances, atoms of oxygen should be bonded with the atoms of the combustible elements not directly, but by the means of atoms of such elements, as nitrogen or chlorine, which are relatively inert to oxygen and to carbon and hydrogen. Otherwise during the formation of molecule, great quantities of heat would be given off and combustible elements partially "burned" already during this formation and the potential energy of ES correspondingly would decrease.

Certain explosive compounds, furthermore, have large density which exceeds the density of explosive mixtures, and the large explosive ability at such densities. Thanks to this density of energy (energy of unit volume) which are larger than for mixtures, that conditions the large destructive force of explosion.

To explosive chemical compounds, in which combustible elements and oxygen are combined substances of number of classes pertain to them. Basic of which and having practical application are complex nitrious ethers of polyatomic alcohols and carbohydrates, which are usually called nitro etters, and nitro compound of aromatic hydrocarbons.

The widest applied are the following nitro esters: glycerine nitrate, usually called by nitroglycerine, $C_3H_5(ONO_2)_3$; ethylene glycol dinitrate, or nitroglycol, $C_2H_4(ONO_2)_2$; diglycol dinitrate $CH_2(ONO_2)CH_2\text{-}O\text{-}CH_2\text{-}CH_2ONO_2$;pentaerythritol tetranitrate (PETN) $C(CH_2ONO_2)_4$; nitrocellulose $[C_6H_7O_2(OH)_{3-n}(ONO_2)_n]_x$.

From nitro compounds in the first place one should name trinitrotoluene $C_6H_2(NO_2)_3CH_3$ (trotyl); poly (di- and tri-) nitronaphthalene $C_{10}H_6(NO_2)_2$, $C_{10}H_5(NO_2)_3$; trinitroxylene $C_6H(NO_2)_3(CH_3)_2$ (xylyl); trinitrophenol $C_6H_2(NO_2)_3OH$ (picric acid).

Also applied are nitramine — trinitrophenyl methyl nitramine $C_6H_2(NO_2)_3NCH_3NO_2$ (tetryl); cyclotrimethylene trinitramine $(CH_2NNO_2)_3$ (hexogen) and cyclotetramethylene tetranitramine $(CH_2NNO_2)_4$ (octagen). Recently significant attention is allotted to nitro derivative and nitramines of fatty and series; from the latest ones it is possible to name ethylene dinitramine $C_2H_4(NHNO_2)_2$ (edna), methylenedinitramine $CH_2(NHNO_2)_2$ (medina) and dinitrate dioxyethylnitramine $O_2NN(CH_2CH_2ONO_2)_2$ (dina).

For ethyl nitrates and nitro compounds, during the explosion all heat or the main part of the heat is given off as a result of oxidation of combustible elements by oxygen. Explosives with negative heat of formation which decompose during the explosion into elements with corresponding liberation of heat, for instance, lead azide PbN_6 are also used.

Explosives, belonging by its chemical structure to a definite class of compounds, possess certain general properties and peculiarities. Thus, a general peculiarity for sensitivity to heating and impact is higher for ethyl nitrates than for nitro compounds of aromatic series; many of them have large heat of explosion due to the large content of oxygen than for usual aromatic nitro compounds, containing three nitro groups in the benzene ring.

However, even within limits of the class, differences between separate representatives can be significant, more so, because certain explosive properties strongly depend not only on its own chemical, but on physical properties, and also on physicomechanical structure of ES. All these properties are considered during the selection of ES for one or another concrete purpose.

Besides classification of belonging to a definite class of chemical compounds, ES by degree of stability of burning and stipulated by its possibilities of application, can be divided into three basis classes: initiating, or primary, secondary (called also explosive, or crushing) and launching (powder).

Chief characteristic of initiating of ES is the fact that their burning is very easily and rapidly changes into detonation. Burning of secondary explosives substances is usually stable and change into detonation only at certain special conditions (porous structure, liquid state, large mass, high temperature and others); therefore, detonation of secondary ES is evoked by not igniting, but by other methods. Burning of launching ES is the stablest and does not change into detonation even during those conditions, at which this transition takes place for secondary ES.

In accordance with the mentioned characteristic conditions of transformation, during technical application of initiating and secondary ES is detonation, but launching ES — burning.

Distinctions in stability of burning of ES of various classes have large practical value. Secondary explosives are prepared and applied in huge quantities. Besides, as shown in practice sometimes ignition of ES can occur. If ignition led every time to explosion, then production of ES would be exclusively dangerous and practically difficult to realize in large scales.

On the other hand, since secondary ES under usual conditions are not able to explode from ignition, another simple and convenient method for practical application is necessary for excitation of their explosion. This method was found about one hundred years ago; it consists in use of capsule-detonator.

Capsuledetonator is the simplest form constituting a shell case with small charges of initiating ES compressed in it. For excitation of explosion charge of secondary ES a capsuledetonator is placed in it and the initiating ES is ignited with the help of ignition cord or electrical current. Initiating ES explodes and excites the explosion of secondary ES.

Initiating ES is significantly more dangerous, since they explode on ignition, and, in general, is much more sensitive to friction and input than secondary ES, but their necessary quantities are incomparably less. Furthermore, initiating substances in large part of industrial process change into moistened state, in which many of them are less sensitive to impact, difficultly ignite and do not give transition of burning into explosion. All this greatly lowers the danger of explosion in the production of initiating ES.

Finally the high stability of powder burning ensures possiblity of application of them in firing weapon. It is clear that under such conditions the initiation of explosion is absolutely impermissible.

With respect to chemical composition of powder, it does not differ from secondary ES. Contemporary nitroglycerine powder consists basically from two typical secondary ES — nitroglycerine and nitrocellulose. High stability of powder burning is caused in the first place by its distinction from the secondary ES with respect to physical properties — viscosity, gas-penetrability (porosity) and durability of powder elements (particles).

CHAPTER II

SLOW CHEMICAL TRANSFORMATION OF EXPLOSIVE SUBSTANCES

§ 1. Basic Forms of Chemical Transformation of Explosive Substances

Chemical transformation of explosives can take place in different forms, of which the basic are: 1) slow chemical transformation; 2) burning and 3) detonation.

Slow chemical transformation is characterized by the fact that, all decomposed substance is at an identical temperature, practically equal to the temperature of surrounding media. The rate of reaction ($-dm/dt$ – derivative of reactant quantity with respect to time) corresponds to this temperature and is identical in all points.* Regularities of slow chemical transformation of ES in principle does not differ from regularities of transformation of nonexplosive substances.

The matter of burning and detonation is somewhat different. Here in both cases there is a front of chemical transformation – relatively narrow zone, where intensive chemical reaction takes place – propagating thru the substance with certain rate. Ahead of

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*Exception constitutes a case, when solid autocatalysts are formed on whose surface the reaction rate is much greater than that in volume.

this zone is the initial ES, and behind it – products of transformation (Fig. 2.1). Temperature T is ahead of the front, behind it and in the actual zone of reaction there is an essential difference, also there is a smaller or larger inequality of pressure p and density ρ.

Reaction rate, more accurately the linear rate of shift in the front of the process (ds/dt – derivative of the path, passed by front, with respect to time), depends basically not on the initial temperature of the substance (environment), but on the quantity of separating energy of the reaction, conditions of its transmission to the unreacting substance and kinetic characteristics which are acquired by it with this transmission of chemical transformation. Since the mechanism of energy transfer during burning and detonation is different, then the rate of propagation is also different and during burning does not exceed (for gases) tens of meters per second, and at detonation constitutes kilometers per second.

Slow chemical transformation, burning and detonation are the basic forms of chemical transformation of explosives. They are interchangeable. Thus, for instance, slow chemical transformation can lead to initiation of burning, burning can pass into detonation. Also intermediate propagation conditions with respect to rate are possible, usually which are transitional and unstable. For certain ES, for instance smoke powder, burning with the rate in several centimeters per second and propagation with speed of about 400 m/sec are known which is too small, for this conditions of propagation to be possibly

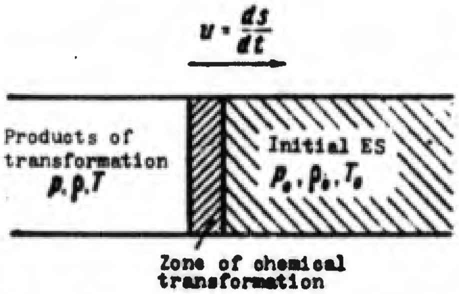

Fig. 2.1. Diagram of self-propagating chemical reaction.

considered as detonation.

In accordance with the rate difference of propagation, the possible mechanical (destructive) action of various forms of transformation of ES is essentially different.

Slow transformation in closed volume by itself, can only lead to increase of pressure until the break of the shell.

Burning can also lead to significant increase of pressure only in closed or semiclosed volume. Correspondingly it is used in those cases, where too large pressures are undesirable (charges of firing weapon).

Detonation, due to the great speed of its propagation, gives maximum pressure (measured by hundreds of thousand of atmospheres), practically not depending on presence or absence of the shell. Correspondingly it is applied when it is necessary to obtain maximum destructive action.

Study of basic forms of chemical reactions taking place in explosives can begin with the consideration of slow chemical transformation. This form of transformation, being the simplest, is at the same time one of the stages of the process of burning and detonation of ES. At the same time the study of slow chemical transformation presents significant interest for resolution of problems of chemical stability of ES.

As was already shown, slow chemical transformation of ES follows the same laws, which characterize the trend of reactions and in nonexplosive systems. Therefore before considering the results, obtained during the study of ES, let us review the basic positions of contemporary kinetics of chemical reactions. This kinetics is developed most fully with respect to gases, giving simple and graphic regularities, which will be considered below.

§ 2. Elements of Kinetics of Simple Gaseous Reactions

1. Mechanism of Chemical Reaction and Dependency of Reaction Rate on Temperature

Let us assume that we have a gas or mixture of gases, capable to bimolecular reaction, for instance mixture of vapors of iodine with hydrogen. In order for molecule of iodine and hydrogen to react, they have to collide with each other. However collision is not sufficient condition for initiation of elementary reaction.

Average time between the collisions of gases at atmospheric pressure is in the order of 10^{-10} sec. If every collision led to elementary reaction then it is simply impossible to obtain a mixture of gases capable of reacting. They would react in the process of mixing.

As it is known, that at ordinary temperature, oxygen does not react with hydrogen. If also at room temperature oxygen is mixed with nitrogen oxide, then the mixture rapidly browns as a result of formation of nitrogen dioxide. Number of collisions between molecules in both cases is approximately equal. Sharp distinction in the reaction rate, shows that it is determined not only with the probability of encountering the reacting molecules.

At present time the generally accepted hypothesis is that of Arhenius, according to which the reaction between molecules occurs only in the case when they are active, i.e. possess during collision certain excessive energy. Such assumption is fully natural, since reaction should precede weakening or destruction of internal bonds of reacting molecules, without which regrouping of atoms is impossible, leading to formation of molecules of reaction products.

In accordance with Arhenius hypothesis the speed of bimolecular reaction, i.e. the number of elementary reactions, occuring for 1 sec., should equal the number of collisions between active molecules, if one were to assume in the simplest case that each of their collision leads to a reaction.

According to the kinetic theory of gases, the number of active molecules in unit of volume is equal to the general number, multiplied on expression $e^{-E/RT}$, where E — excess energy of active molecule. Thus, if reaction takes place according to the diagram

for instance,

$$M+M=L+P,$$

$$HJ+HJ=H_2+J_2,$$

and if the concentration of molecules M designated by [M], then general number of collisions Z among these molecules according to the kinetic theory, will be determined by expression

$$Z=\frac{\sqrt{2}}{2}\pi\sigma^2\bar{u}[M]^2, \qquad (2.1)$$

where σ — diameter of molecule M;

$\bar{u}$ — average speed of its motion.

Let us designate by $[M_1]$ the number of molecules M possessing an energy exceeding a certain magnitude E_1. It is obvious that

Correspondingly,

$$[M_1]=[M]e^{-E_1/RT}.$$

$$[M_2]=[M]e^{-E_2/RT}.$$

Assuming that $E_1 + E_2 = E$, where E — activation energy of a given reaction; then the number of collisions between molecules, satisfying these conditions,

$$Z_1=\frac{\sqrt{2}}{2}\pi\sigma^2\bar{u}[M_1][M_2]=\frac{\sqrt{2}}{2}\pi\sigma^2\bar{u}[M]^2e^{-E/RT}.$$

Thus, the number of collisions, at which the sum of energies of colliding molecules is equal or exceeds the activation energy, equal to the general number of collisions between molecules of reagents, multiplied by fraction $e^{-E/RT}$.

At above-indicated assumption the speed of reaction w (number of molecules, reacting for 1 sec. in 1 cm^3) is equal to the doubled number of collisions, at which the total energy of colliding molecules exceeds the activation energy

$$w = \sqrt{2}\pi\sigma^2\bar{u}[M]^2 e^{-E/RT}. \qquad (2.2)$$

Expression (2.2) can be rewritten in the following form:

$$w = K[M]^2, \qquad (2.2a)$$

where

$$K = \sqrt{2}\pi\sigma^2\bar{u}e^{-E/RT}.$$

If the products of first four factors, not depending or weakly depending on temperature, is designated B, then

$$K = Be^{-E/RT}. \qquad (2.3)$$

Value K is a constant, characterizing the dependency of the reaction rate on temperature, determined by value E. The larger the activation energy, the stronger the reaction rate is increased with increase of temperature.

Conforming to this formula, by experimental data it is possible to check by following means.

Logarithm of expression (2.3), is

$$\ln K = -\frac{E}{R}\frac{1}{T} + \ln B. \qquad (2.4)$$

Since second member of right side in the first approximation does not depend on temperature, then (2.4) can be rewritten in the following form:

$$\ln K = -\frac{E}{R}\frac{1}{T} + \text{const.} \qquad (2.4a)$$

Consequently, logarith of the rate must be related to the reverse absolute temperature by linear dependency. Constructing by experimental data of graphics ln K - $\frac{1}{T}$, we have to obtain straight line. This dependency is fulfilled for majority of reactions (see, for instance, Fig. 2.2).

Let us consider shortly the question about the nature of active molecules. Fast molecules in the first place, can be active molecules, having kinetic energy, equal or exceeding activation energy E.

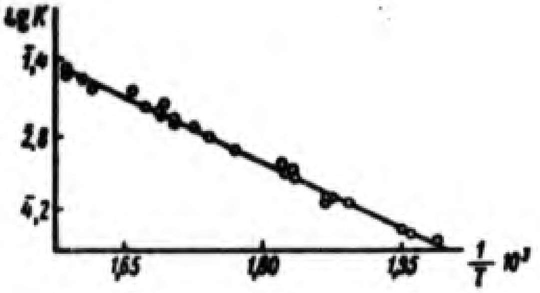

Fig. 2.2. Dependency of constant K speed of thermal disintegration of ethylene-diamine dinitrate on temperature T.

Forces, appearing at the moment of collision of such molecules, surmount their relative stability and make reaction possible. For weakening of initial bonds between atoms in initial molecules, and also for surmounting of repulsion between approaching molecules, energy must be expended regardless of whether the reaction is exothermic or endothermic.

Let us explain the role of activation by the following analogy. Let us assume that carriage stands on the hill in position a (Fig. 2.3). Although on level b position of carriage would be stabler in accordance with lower level of potential energy, which is decreased into heat of reaction Q, they nevertheless are not rolled. Hill ac does not allow them to move downwards and makes their position relatively stable. A push is necessary which would lift the energy of carriage to magnitude E to a level c, after which they will be rolled downwards by themselves. Kinetic energy can play the role of this push during the interaction of molecules.

Besides fast forms there are possible other forms of active molecules. In known conditions (absorption of light impact of electron or molecule) energy; obtained by molecule, can be expended for shift of one of peripheral electrons from normal orbit to orbit corresponding to large potential energy relatively to the remaining part of the molecule. In this state molecules are called excited; as is shown by the experiment, they can be active in the sense of Arhenius hypothesis.

At last, there exists a third form of active particles: free atoms or radicals. Decomposition of molecule into atoms or radicals is related to more or less significant expenditure of energy, which in the potential form (in form of chemical energy) is contained in the form of particles of molecule and conditions their increase in reactivity. Such particles, having uncoupled electron, are characterized by unsaturation of valence and easily, with very low activation energy, enters in reaction of bonding.

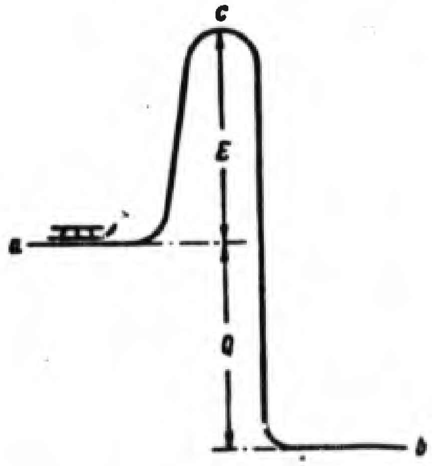

Fig. 2.3. Energy level diagram of molecule, preactivation (a), after activation (c) and after reaction (b).

As examples it is possible to show the reaction of atomic hydrogen with halogens:

$$H + Cl_2 = HCl + Cl + 45.0 \text{ kcal};$$
$$H + Br_2 = HBr + Br + 40.5 \text{ kcal};$$
$$H + J_2 = HJ + J + 33.7 \text{ kcal}.$$

These exothermic reactions require very small activation energies (corresponding to 0.3; 0.1 and 0.0 kilocalories/mole). Even at room temperature substitution occurs practically during every collision of atom of hydrogen with molecule of halogen. Reactions of molecular hydrogen with halogens takes place incomparably more difficultly: for instance, reaction between hydrogen and iodine has an activation energy of 40 kilocalories; correspondingly its speed at room temperature is practically equal to zero.

2. Dependency of Reaction Rate on Concentration (Pressure); Change of Speed with Respect to Time

Speed of reaction, as we saw, is proportional to the number of collisions between active molecules. Number of collisions is proportional to the product of concentrations of substances, participating in reaction, i.e., if gases react formation of their partial pressures.

In general form for reaction, proceeding by equation

$$n_1A_1+n_2A_2+n_3A_3+\ldots=X,$$

where X — product of reaction, dependency of rate on reagent concentrations can be expressed by the following form:

$$\frac{dx}{dt}=Ka_1^{n_1}a_2^{n_2}a_3^{n_3}, \qquad (2.5)$$

where the concentration of reactants are designated by a_1, a_2, etc., and the final product — through x.

Dependency (2.5) determines also the change of rate with respect to time, if concentration of reagents change during the reaction proven. Last condition is executed for reactions in gas phase and in solutions. Concentrations of reactants in time decrease and speed of reaction drops. This drop occurs in different ways, depending upon the number of molecules, participating in the reaction.

In the case when $n_1 = 1$, and $n_2, n_3 \ldots = 0$ (reaction of first order), expression (2.5) will take form

$$\frac{dx}{dt} = Ka_1. \qquad (2.6)$$

If initial concentration of parent substance is designated by a, then

$$a_1 = a - x$$

and

$$\frac{dx}{dt} = K(a-x)^{*}. \qquad (2.7)$$

Dividing variables and integrating, we obtain

$$\ln\frac{a}{a-x} = Kt, \qquad (2.8)$$

or

$$K = \frac{1}{t}\ln\frac{a}{a-x}. \qquad (2.9)$$

Rate constant K has the dimension t^{-1}, and its value depends only on selected unit of time. If it, as usually, is expressed in seconds, then dimension of constant – reverse seconds ($sec.^{-1}$).

Dependency of concentration x of reacting substance with respect to time, we find from expression (2.8):

$$x = a(1 - e^{-Kt}). \qquad (2.10)$$

Differentiating equation (2.10), we obtain dependency of reaction

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*Relationship (2.7) is executed also in case, when liquid or solid matter, reacting, completely is turned into gases. In these conditions concentration of parent substance does not change, but the speed of gas generation in time decreases by reaction equation of the first order. In this case fulfillment of equation (2.7) indicates only on the fact that decomposition rate is proportional quantity of available substance and does not discuss the order of reaction.

rate with respect to time:

$$\frac{dx}{dt}=aKe^{-Kt}. \qquad (2.11)$$

Graphically these relationships are depicted by curves Fig. 2.4 and 2.5.

Let us note one more relationship, frequently utilized for establishment of reaction order.

From expression (2.8) let us determine the half-life $t_{1/2}$, i.e. time, during which half of parent substance will react $(x = a/2)$;

$$t_{1/2}=\frac{1}{K}\ln 2. \qquad (2.12)$$

Thus, for monomolecular reactions, time of transformation of half (or any other part) substance does not depend on its initial concentration.

For reaction of the second order $(n = 2)$, in which participate two molecules (bimolecular reactions), differential kinetic equation (at equal initial concentrations of both reagents) has following form:

$$\frac{dx}{dt}=K(a-x)^2. \qquad (2.13)$$

After integration we obtain

$$\frac{x}{a(a-x)}=Kt. \qquad (2.14)$$

Magnitude of rate constant K, in distinction from reaction of first order, depends on the unit of concentration measurement. If concentration is expressed in moles per liter, but time in seconds, then K will have dimension liter mole^{-1} sec^{-1}.

From expression (2.14) find

$$t_{1/2}=\frac{1}{K}\frac{1}{a}. \qquad (2.15)$$

In this case half-life depends on initial concentration, and namely, its reciprocal.

Reactions of first and the second order embrace practically all real processes; reaction of third, and the higher orders are extremely rarely.*

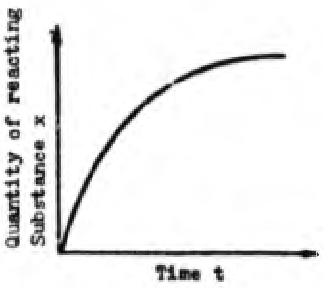

Fig. 2.4. Dependency of quantity x of reacting substance during monomolecular reaction with respect to time t.

Factor B in equation (2.3) in the case of bimoleculer reactions is numerically equal to doubled quantity of collisions between molecules for 1 sec. in unit of volume; at reagent concentrations 1 mole/liter, this factor according to calculation is equal ~10^{11}.

A number of reactions are known, for which good conformity of reaction rate value is obtained, determined experimentally, and the rate, calculated by equation (2.2). However in certain cases actual rate of reaction is much less than the calculated, and in the expression of constant of speed (2.3) it is necessary to introduce a correction factor P, so-called <u>probability factor</u>, magnitude of which is from 1 to 10^{-7}. Magnitude of P can depend on a number of reasons: for instance, the influence of geometry of molecules on effectiveness of collisions, since molecule of products that are rich in energy are strongly exothermic reactions and can decompose before they are able to lose this energy,

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*This does not mean that dependency of reaction rate on concentration is always expressed by its proportionality of the first order or square (product) of concentration. In many complicated reactions the total speed of the process is proportional to the concentration of the initial products in the order, different from 1 or 2.

therefore the duration of collisions may be insufficient for redistribution of energy, and etc.

Less clear is the question on the mechanism of monomolecular reaction and on the physical meaning of pre-exponential factor B in this case.

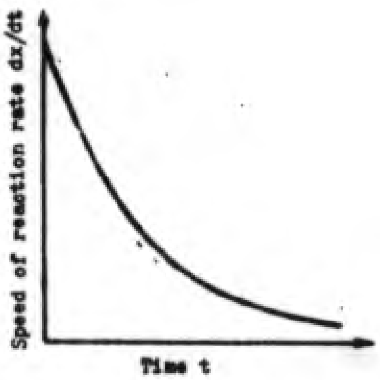

Fig. 2.5. Dependency of speed dx/dt monomolecular reaction with respect to time t.

Basic difficulty consists in the following. For elementary monomolecular reaction to take place, and molecules entering it should obtain activation energy. This energy molecule obtains as a result of exchange by energy during collisions with other molecules. Number of activating collisions which is proportional to the general number of collisions, i.e. square of concentration. Thus, the number of active molecules, forming into unit of time, is proportional to the square of concentration. At the same time the number of decomposing molecules (rate of reaction) is proportional to the first order of concentration.

This apparent contradiction is explained by the following. Activated molecule as a result of collision does not decompose immediately. If the time of its existence τ is greater than the time between collisions τ_0, then the large part of active molecules is deactivated during subsequent collisions, before the molecule succeeds in decomposing. As a result of deactivation an equilibrium is established between the active and not active molecules, in other words, a certain definite concentration of active molecules is established for given temperature. The number of composing molecules is proportional to the concentration of active molecules and, consequently, concentration of substance in first order.

According to this explanation the reaction rate should remain proportional to the first order of concentration only then, when $\tau \gg \tau_0$. If we decrease the number of collisions at a given temperature; for instance, decrease of gas pressure, then it is possible to increase the time τ_0 between collisions to such an extent, so that all active molecules will be able to decompose in time, prior to their subjugation to deactivating collisions. Then the reaction rate will be proportioned to the number of activating collisions, i.e., square of the concentration.

By designating the initial molecules by A, active molecules A' and the reaction product by X it is possible to write:

$$\begin{array}{rl} A + A \underset{K_2}{\overset{K_1}{\rightleftarrows}} A + & A'. \\ & \downarrow K_3 \\ & X \end{array}$$

In the state of equilibrium

$$\frac{d[A']}{dt} = K_1[A]^2 - K_2[A'][A] - K_3[A'] = 0,$$

where

$$[A'] = \frac{K_1[A]^2}{K_2[A] + K_3}.$$

The rate of formation of reaction product X is equal $K_3[A']$, therefore

$$\frac{dx}{dt} = \frac{K_3K_1[A]^2}{K_2[A] + K_3}.$$

If [A] is large and $K_2[A] \gg K_3$, then $\frac{dx}{dt} \approx \frac{K_1K_3}{K_2}[A]$, i.e. the reaction rate is proportional to the first order of concentration.

If [A] is small, and $K_2[A] \ll K_3$, then $\frac{dx}{dt} \approx K_1[A]^2$, i.e. reaction rate is proportional to the square of concentration.

These theoretical conclusions are confirmed by experiment. With decrease of pressure below the known limit, the monomolecular reaction rate ceases to be changed proportionally to the first order of pressure (concentration) and at sufficiently small values of the latter it exactly follows the reaction equation of the second order.

Considered explanation is in accordance with the fact that usually only complex molecules, consisting of several atoms are capable monomolecular decomposition. Significant number of bonds are present in them, by which the general reserve of energy can be distributed.

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For understanding the mechanism of self-propagation of exothermic reaction, it is necessary to consider simplest case of self-accelerated reaction — the case of macrohomogenous process.* Self-spreading reaction can be considered as consecutive passage in adjacent layers of substance of macrohomogeneous self-accelerated reaction, occurring at conditions of obtaining of energy from preceding reacting layer and its yield to the subsequent layer.

Let us consider three basic mechanisms of autoacceleration reaction: thermal, autocatalytic and chain.

1. Thermal autoacceleration occurs due to self-heating up of a system at the expense of heat separated during reaction.

2. Autocatalytic, or, more exactly, autocatalytically-thermal autoacceleration occurs as a result of accumulation of reaction products, catalyzing transformation of the starting substance. When preponderance of heating is above the heat loss is attained thermal acceleration sets in and is finished by explosion. Autoacceleration reaction pertains here as a result of accumulation of intermediate product during the decomposition in several consecutive stages.

3. Chain autoacceleration reaction at constant temperature occurs as a result of excessive branching above the break of chains.

In many cases of chain reactions development, heat loss may be insufficient for drawing away of all reaction heat; then the heat

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*Macrohomogeneous is such a reaction, when the average speed of transformation in certain not too small volume of element is identical. For self-propogating reaction, at which the surface, more accurately the zone of front, divides whole volume into two parts — unreacting substance and products of reaction, — this condition is not fulfilled. Macrohomogeneous reaction may be micro-heterogeneous, as this has been the case, for instance, during topochemical reaction in solid matter, where chemical transformation starts in separate points, from which it spreads in the form of growing embryos.

is joined to the chain acceleration and autoacceleration becomes chain heated on initial increase of reaction rate, occurring due to branching of chains, thermal acceleration is added; joint action of both mechanisms leads to explosion.

For exothermic gas reactions are real and all three mechanisms of autoacceleration are studied. For condensed explosive systems, it is essential for the existence of autocatalytically-thermal, and apparently, also pure thermal autoacceleration. Indisputable experimental proofs of chain mechanism of slow preexplosive chemical transformation, and consequently the chain mechanism for initiating explosion for condensed systems has not been obtained.

It is possible that the presence of chains of significant length during usual or moderately raised temperatures would be related with the very great ease of explosion, initiation, which is even larger than, for instance, nitrogen chloride for which the chain reaction and chain explosion (in pairs) are fixed experimentally.* Such ES, due to their excessive explosive danger, have remained practically unstudied.

1. Thermal Autoacceleration of Reaction (Thermal Explosion) in Gases

Thermal acceleration of reaction and appearance of explosion occur as a result of increase in temperature of reactant at the expense of heat of the actual reaction.

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*Let us note that for chain reaction of nitrogen chloride decomposition, upper limit of pressure is observed, i.e., the explosion ceases on increase of vapor concentration to relatively small values, much smaller than the concentration of substance in liquid nitrogen chloride.

Qualitative picture of thermal acceleration of reaction and appearance of explosion was formulated in 1884 by Vant-Hoff by the following form (Fig. 2.6).

If at certain point of inert medium a local heating is caused (for instance, transmission of electrical spark), then the heat will spread from layer to layer, where in every following layer the maximum temperature will be lower than in the preceding (Fig. 2.6a).

If moderate heating is created in the medium, which is capable of exothermic reaction, then also a drop of temperature will be observed, but much slower, since heat loss of each layer in certain measure will be compensated by liberation of heat during the reaction (Fig. 2.6b).

During strong heating the reaction rate can become so great that at the expense of liberation of heat of reaction temperature, from layer to layer will not drop, but will increase and ignition will occur (Fig. 2.6c).

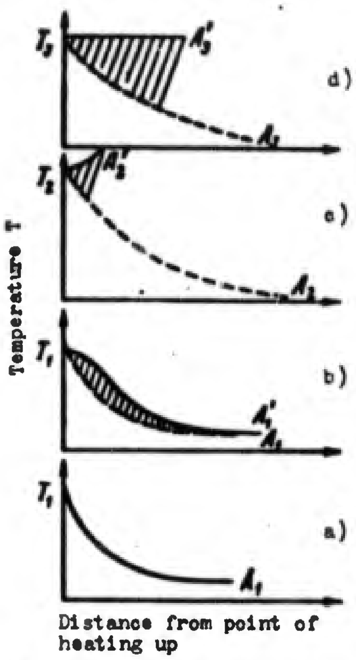

Fig. 2.6. Diagram of thermal ignition according to Vant-Hoff.

Minimum temperature T_3 (Fig. 2.6g), starting from which this occurs, is its own kind of limit, separating the region of ignition from the region of slow attenuating reaction in given conditions of its process. This is the temperature of ignition of explosive system.

If ignition appears without igniting from without, but at the expense of temperature rise, to which all system is evenly heated, then we speak of self-ignition or flash.

The simplest method of determination of temperature self-ignition of gases, offered by Le Chatelier, consists of that, which the investigated gas is admitted into evacuated vessel, preliminarily heated to a definite temperature. Increasing temperature of the vessel during successive experiments the minimum value is established, starting from which is observed the ignition of gas. To deficiencies of this method pertain: the possibility of noticeable change of gas composition at the expense of reactions, passing during its heating to the temperature of vessel, and the flow of heterogeneous reactions at the hot wall.

In the method of Dikson coaxial tubes, developed for determination of temperature of self-ignition of mixtures, each of the gases, passing thru the tube, is preheated and they are mixed in the hot state.

In the method, offered by Nernst, gas heating is produced by its adiabatic compression. Since compression occurs rapidly and the wall of the vessel are initially cold, the preardent and heterogeneous reactions lead to a minimum.

In Table 2.1 are given temperature of self-ignition of certain combustible gases in mixture with air at atmospheric pressure.

Quantitative theory of thermal self-ignition was developed in 1928 by N. N. Semenov, who, as Vant-Hoff, originated from the presentation of slow exothermic reaction taking place, which is accelerated with increase of temperature.

Let us consider explosive gas (or mixture of gases), that is in a vessel. At certain values of initial temperature and pressure, heat which separates during slow reaction, does not succeed under given conditions of heat withdrawal to be drawn out through the walls of vessel and thus heats the gas. Due to this heating, reaction is accelerated, and acceleration of the reaction increases heating that still further accelerates the reaction and etc. Thus, the progressive self-heating of mixture and autoacceleration of reactions proceeds leading to self-ignition.

Table 2.1. Temperature of Self-Ignition of Mixture of Certain Gases with Air

Gas	Temperature of self-ignition °C	Gas	Temperature of self-ignition °C
Hydrogen	530	Ethylene	540
Carbon dioxide	610	Propylene	455
Methane	645	Butene	445
Ethane	530	Acetylene	335
Propane	510	Carbon disulfide ...	290
Butane	490	Illumination gas ...	560

Let us assume that a vessel has a constant temperature T_0. Obviously, the larger will the pressure be (more exact, concentration) of a gas or mixture of gases, the bigger will the reaction rate be, and consequently the heat gain in unit of time. Speed of abstraction of heat does not depend on pressure. Therefore at sufficiently small pressures, heat gain cannot be larger than the heat withdrawal and the reaction will flow at practically constant temperature, close to temperature of the vessel. Due to increase of pressure, gas admitted into the vessel, increases the reaction rate and the heat gain and heat withdrawal remains constants. It is obvious that for a given initial temperature there exists a minimum pressure, at which heat gain becomes equal heat withdrawal. At higher pressures the heat gain exceeds the heat withdrawal; temperature of admitted gas into the vessel in this case continuously grows leading to self-ignition.

Analogously for a given pressure of gas there exists a certain minimum temperature of the vessel, below which a chemical transformation flows in the form of slow reaction, and higher — leads to self-ignition.

Problem is brought to the determination of minimum temperature for pressure p_0, i.e. dependency between pressure of gas and minimum temperature, leads to self-ignition.

Let us clarify what has been said by the graph. On Fig. 2.7 curve gives heat gain q_1 as a function of temperature at given pressure p_0. Straight lines 1, 2, and 3 give correspondingly for three different temperatures of vessel T_0', T_0, and T_0'' heat withdrawal q_2, which, as was shown, does not depend on pressure.

Let us see how will reaction flow at different temperatures of the vessel. Cold gas, admitted into the vessel with temperature T_0', will be heated to this temperature. Since at T_0', heat loss is equal to zero, but heat gain has a certain finite value q_1', then the gas will continue to be heated to temperature T_1'.

At a temperature T_1' heat gain and heat loss are equal among themselves. It is not difficult to show that this equilibrium is stable. Actually, if for any reason the temperature of gas is brought higher than T_1', then heat loss will become larger than the heat gain and the temperature will drop to T_1'. Thus, the reaction will flow without acceleration at a temperature T_1'.

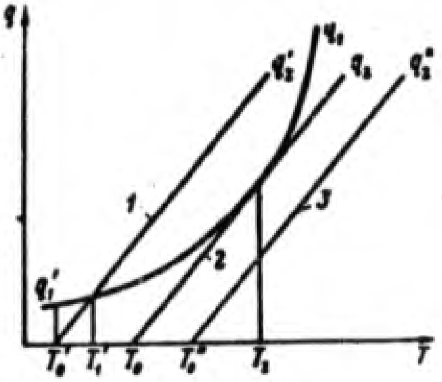

Fig. 2.7. Thermal explosion according to Semenov.

If the vessel has higher initial temperature, for instance T_0'', then line 3 for heat loss will wholly lie below the curve of heat gain. Repeating the same reasoning, we will be convinced that the temperature of the gas, admitted into the vessel, will continuously grow and the experiment will be completed by self-ignition.

Temperature T_0 of the vessel presents a limited case between slow reaction and self-ignition. Straight line 2 for heat loss in this case only concerns the curve of heat gain and is sufficiently very small variation in temperature of the vessel in one or the other side, in order for explosition to take place or for quiet flameless reaction. This temperature T_0 will be, obviously, minimum temperature, leading to explosion at given pressure p_0 of the gas.

Mathematical connection between the minimum temperature and pressure is found by the following calculation.

If in the gas phase a reaction takes place with speed w, measured by the number of molecules of the product, appearing in 1 sec. in a unit volume, then the quantity of heat, separated every second in the whole volume v vessel, is equal to

$$q_1 = w\frac{Q}{N}v. \tag{2.16}$$

Here Q is the heat, separated during formation 1 g-mole of product;

N is Avogadro number.

The reaction rate as a function of temperature T and number of molecules of the starting compound in unit of volume a and in the initial stage is equal: for monomolecular reaction

$$w_1 = B_1 a e^{-E/RT};$$

for bimolecular reactions

$$w_2 = B_2 a^2 c^{-E/RT}.$$

Considering in the first approximation that temperature of gas in all points inside vessel is identical and abtraction of heat to the outside is caused by heat transfer from gas to walls of vessel. It is possible to determine the quantity of heat q_2, given off in 1 sec. from the reaction space:

$$q_2 = \alpha(T - T_0)S. \tag{2.17}$$

Here α — heat-transfer coefficient;

T — temperature of reacting gas;

T_0 — temperature of walls of vessel, equal to temperature of the external medium;

S — surface of vessel.

Dependency (2.17) will be expressed by straight line, identical for various pressures, if it is considered that α does not depend on pressure.

As can be seen from Fig. 2.7, if the temperature of the vessel is equal T_0, then curve of heat gain touches straight line of heat loss. Mathematically the condition of contact can be expressed as equality at point of contact of ordinates of curve and straight line and their derivatives:

$$q_1|_{T=T_2} = q_2|_{T=T_2}; \tag{2.18}$$

$$\left.\frac{dq_1}{dT}\right|_{T=T_2} = \left.\frac{dq_2}{dT}\right|_{T=T_2}. \tag{2.19}$$

Placing expression for q_1 and q_2 in equations (2.18) and (2.19), we obtain for monomolecular reaction

$$\frac{vQBae^{-E/RT_2}}{N} = \alpha(T_2 - T_0)S; \tag{2.18a}$$

$$\frac{vQBaE}{NRT_2^2}e^{-E/RT_2} = \alpha S. \tag{2.19a}$$

In these equations, besides known temperature T_0, enters temperature T_2, corresponding to point of tangency, which at usual setting of experiment we directly do not determine.

More detailed analysis of Senenov showed that at those values of activation energy and temperature of self-ignition, which characterize explosions of gas mixtures, T_2 is very close to T_0.

Therefore we consider in denominator of equation (2.19a) $T_2^2 \approx T_0^2$; in exponential function ($e^{-E/RT}$) consideration that $T_2 > T_0$, leads to appearance before this function of factor e.

Thus, condition of self-ignition will obtain in the form

$$\frac{Q v B a E e}{N R T_0^2 \alpha S} e^{-E/RT_0} = 1. \tag{2.20}$$

Number of a molecules in unit of volume is related with pressure p by the following relationship:

$$p = \frac{aRT}{N} \frac{\text{dyne}}{\text{cm}^2} = \frac{aRT}{N} 10^{-6} \text{ megabar } = \frac{aRT}{N} 10^{-6}\, 750 \text{ mm. of Hg.}$$

where $R = 8.314 \cdot 10^7$ erg/deg and $N = 6.023 \cdot 10^{23}$.

Hence pressure, expressed in millimeters of Hg

$$p \approx aT \cdot 10^{-19},$$

whence

$$a \approx \frac{p}{T} 10^{19}. \tag{2.21}$$

Placing expression (2.21) in (2.20), we obtain relation between pressure p_0 gas and minimum temperature of self-ignition:

$$\frac{Q v B p_0 E e \cdot 10^{19}}{N R T_0^3 \alpha S} e^{-E/RT_0} = 1, \tag{2.22}$$

or

$$\frac{p_0}{T_0^3} = \frac{N R \alpha S}{Q v B E e \cdot 10^{19}} e^{E/RT_0},$$

whence

$$\lg \frac{p_0}{T_0^3} = \frac{E \lg e}{R} \frac{1}{T_0} + \lg \frac{N R \alpha S}{Q v B E e \cdot 10^{19}},$$

or

$$\lg \frac{p_0}{T_0^2} = A \frac{1}{T_0} + B, \qquad (2.23)$$

where

$$A = \frac{\lg e \cdot E}{R} = 0{,}217E;$$

$$B = \lg \frac{N R_0 S}{Q_0 B E e \cdot 10^{10}}.$$

For bimolecular reaction by analogous conclusion we obtain

$$\lg \frac{p_0}{T_0^2} = \frac{A}{T_0} + B, \qquad (2.24)$$

where A = 0.11E.

Since there are possible different mechanisms of autoacceleration of reaction to explosion, then during investigation of concrete system it is necessary to establish, which mechanism is the determining one. That circumstance which is found during experimentation of value for minimum pressure and absolute temperature of self-ignition, satisfy the relationships (2.23) or (2.24), and cannot serve as unconditional proof of thermal nature of self-ignition for a given system. What does a more detailed consideration show and in case of autoacceleration of reaction by other mechanisms (chain, autocatalytic, see below) is similar or close to it dependency between minimum pressure and initial temperature, necessary for self-ignition obtained.

During thermal self-ignition, minimum pressure should depend on the diameter of the vessel, since with decrease of diameter relation of vessel surface to volume, and consequently also relation of heat loss to heat gain increases. However, even this dependency is not characteristic only for thermal self-ignition. As we will see below, decrease of diameter during chain reaction development can lead to decrease of its rate, although even by other cause.

The only reliable means of establishing of thermal mechanism of self-ignition for a given reaction, according to Semenov, is the following. It is necessary to study kinetics of slow reaction and to determine the coefficient of heat loss at various pressures and temperatures. Placing the obtained dependencies into equation

$$\lg \frac{p}{T_0^2} = \frac{A}{T_0} + B.$$

one can determine the value A and B. If these values coincide with values, obtained during direct explosive experiments, then this indicates to the reality of thermal mechanism of self-ignition for a given case.

Thermal mechanism is established for self-ignition for a number of gases and gas mixtures during heating (azomethane, methylnitrate, nitrous oxide, hydrogen sulfide with oxygen). In these cases the dependency is fullfilled.

$$\lg \frac{p}{T_0^2} = \frac{A}{T_0} + B$$

and value A and B, found during experiments with explosion, will agree well with the calculated according to kinetic data for slow reaction.

On the degree of this conformity it is possible to judge, comparing minimum temperatures of self-ignition, obtained by calculation and by experimental means (Table 2.2).

Table 2.2. Calculating and Observed Temperatures of Self-Ignition of Azomethane, Methylnitrate, Mixture of Hydrogen Sulfide with Oxygen and Nitrous Oxide

Azomethane $(CH_3)_2N_2 \rightarrow C_2H_6 + N_2$

p mm. of Hg.	18	22,5	28	31	38	55	67	102	191
T_{calc} °K	656	653	649	647	644	638	635	629	619
T_{obs} °K	659	651,2	644,9	643,4	636,4	630.7	626.3	620	614

Continuation of Table 2.2.

Methylnitrate $2CH_3ONO_2 \rightarrow CH_3OH + CH_2O + 2NO_2$

P mm. of Hg.	4,2	5,5	8,5	12,5	16,5	33,5	45,4	87,0	107,0	163,0
T_{calc} °K	590	586	578	572	566	556	551	541	538	531
T_{obs} °K	597	584	567	553	546	534	529	522,5	521	519,5

Mixture of hydrogen sulfide with oxygen $2H_2S + 3O_2 \rightarrow 2H_2O + 2SO_2$

P_{tot} mm. of Hg.	244	400	745
P_{H_2S} мм	98	160	298
T_{calc} °K	544	523	499
T_{obs} °K	578	552	525

Nitrous oxide $2N_2O \rightarrow 2N_2 + O_2$

P mm. of Hg.	170	330	590
T_{calc} °K	1255	1175	1110
T_{obs} °K	1285	1195	1100

During admission of gas into the vessel self-ignition occurs with certain delay. For gases, given in Table 2.2, it was established that magnitude of this delay at various temperatures and pressures will agree with thermal theory.

2. Thermal Autoacceleration of Reaction in Condensed ES

In examining of thermal self-ignition in gases, it was assumed that transmission of heat occurs only by means of convection. For solid compounds, but in known degree also for liquids this assumption is inapplicable.

Frank-Kamenetskiy observed thermal autoacceleration of reaction and self-ignition in the case, when heat is transmitted only by means of thermal conduction. Equation of heat balance for steady state of infinitely extended flat layer of ES with thickness of 2d at a temperature of environment T^oK has the form

$$\eta\left(\frac{d^2\theta}{dx^2}\right)+qBe^{-E/R(T+\theta)}=0, \qquad (2.25)$$

where x — coordinate, counted off from plane of symmetry of layer;

η — thermal conduction;

q — heat of reaction to unit of volume of ES;

θ — difference of temperatures of ES and environment.

On surface of layer, i.e. at $x = \pm d$, this difference is taken to equal zero. In middle of layer, i.e. at $x = 0$, magnitude θ has the biggest value.

Frank-Kamenetskiy showed that stable equilibrium between heat gain and heat loss becomes impossible at condition, if the parameter is dimensionless

$$d^2\left(\frac{q}{\eta}\right)Be^{-E/RT}\frac{E}{RT^2}>0.88. \qquad (2.26)$$

For cylinder of critical value of this parameter constitutes 2.00; for sphere 3.32.

For solid ES relationship (2.26) are applied directly; in liquid ES heat transfer is carried out partially by convection, relative role of which depends on viscosity, and also on stirring of liquid by bubbles of separating gases. Correspondingly, increase of effective heat-transfer coefficient a critical value of Frank-Kamenetskiy parameter will be in this case larger than during transmission of heat only by thermal conduction.

Check of these presentations was conducted by Ridil and Robertson using as example, nitrocellulose, hexogen and TENA. Layer of nitrocellulose of thickness 0.5 mm. between two copper plates ignites, starting from 213°. On the basis of data on heat and rate of slow decomposition of nitrocellulose, the rate of heat emission 213° is equal to 8.25 cal/cm^3 sec. activation energy of 47,000 cal/mole and taking $\eta = 3 \cdot 10^{-4}$ cal/cm sec deg., we obtain Frank-Kamenetskiy parameter equal to 1.7, i.e. only twice as large than the theoretical value. This may be caused by inaccuracy of certain data, used for calculation.

For a hexogen layer of 0.4 mm. thickness the temperature of flash was 260°C at atmospheric pressure. If one were to take the rate constant of decomposition $K = 10^{18.5} e^{-47,500/RT}$, heat of reaction (by composition of decomposition products) equal to 191 kilocalories/mole, or 1000 cal/cm^3, density 1.2 g/cm^3 (taking into account the presence of bubbles) and value η equal to thermal conduction of liquid ES ($3 \cdot 10^{-4}$ cal/cm sec deg), then the critical parameter will be equal 12, i.e. significantly larger than the theoretical value. Thus, one should assume that at the expense of convection and stirring rate of transmission of heat is increased to 13 times as compared to the rate of transmission by thermal conduction.

For TENA analogous experiment at a layer thickness of 0.13 mm. gave a flash temperature of 240°; at the heat of reaction 74 kilocalories/mole gives a value of critical parameter, equal 2.2, i.e. much closer to the theoretical than for hexogen.

Thus, experimental data on self-ignition of certain condensed ES during heating in general satisfactorily agree with theory of thermal explosion.

3. Autocatalytic Acceleration of Reaction (Autocatalytic Explosion)

As it is known, a catalyst is a substance, with variable speed of reaction, but remaining the same quantity after reaction as at the beginning.

The simplest and general explanation of homogeneous catalysis consists in that, that catalyst enters with catalyzed substance into intermediate reactions, which take place significantly faster than the non-catalyzed reaction. If substance X catalyzes reaction $A \rightarrow B$, then flow of reaction in presence of a catalyst can be presented, as a sum of two consecutive reactions:

$$A+X\rightarrow AX \text{ and } AX\rightarrow B+X,$$

proceeding with smaller energies of activation than non-catalyzed reaction. In many cases insignificant concentrations of catalyst evoke very significant change of reaction rate.

If the catalyst is a product of reaction, final or intermediate, then such reaction is called autocatalytic. Speed of reaction in this case is increased by measure of its flow as a result of accumulation of the catalyst passes through maximum and starts to drop due to decrease of quantity of the starting substance, when influence of this decrease no longer is compensated by growth of concentration of the catalyst. The maximum velocity depends on relationship of constants of speed. If primary reaction is monomolecular and its constant is K_1, and the speed of autocatalytic reaction is proportional to the concentration of reaction products in the first degree and its constant is K_2, then at different relations K_2 to K_1 curves of change of speed in time have the form, shown in Fig. 2.8.

When autocatalytic reaction takes place in the solid phase, it differs by certain peculiarities, caused by immobility of solid products; which catalyze the process. Process in this case obeys either the general dependencies, of the peculiar chain reactions, or the specific regularities (topochemical reactions), which will be considered in the following division of this paragraph.

Let us consider homogeneous autocatalysis by the final products.

During homogeneous autocatalysis in liquid phase the total reaction rate can be presented in the form

$$w = w_1 + w_2,$$

where w_1 – speed of reaction, not depending on concentration of catalyst, for instance monomolecular;

w_2 – speed of autocatalytic reaction.

In the simplest case, the speed of autocatalytic reaction is proportional to the first degree of concentration of autocatalyst.

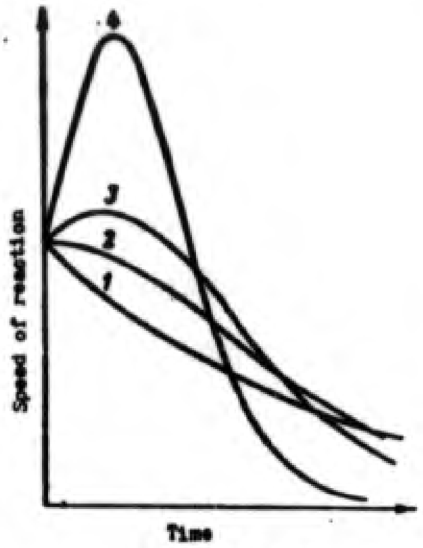

Fig. 2.8. Change of speed of autocatalytic reaction with respect to times.

Curves: 1) $\frac{K_2}{K_1} = 0$; 2) $\frac{K_2}{K_1} = 1$; 3) $\frac{K_2}{K_1} = 2$; 4) $\frac{K_2}{K_1} = 5$.

If the total amount of liquid phase in the course of process is not changed and concentration of catalyst x is proportional to the quantity formed, then for that case it is possible to write

$$\frac{dx}{dt} = K_1(a-x) + K_2x(a-x). \qquad (2.27)$$

From relationship (2.27) it is clear that if we talk about the small changes in the degree of decomposed substance, when by decreasing (a - x) it can be neglected, and the catalyst possesses great effectiveness, then the decomposition rate approximately is determined by relationship

$$\frac{dx}{dt} \approx K_2x,$$

and its dependency on time – by model equation

$$\frac{dx}{dt} \approx e^{K_2t}.$$

Conversely, if decomposition takes place at large concentration of the catalyst, then the decomposition rate will drop according to monomolecular law, but its constant – is the constant of the catalytic reaction.

From expression (2.27) it is easy to obtain

$$\frac{dx}{dt}=K_2\left(\frac{K_1}{K_2}+x\right)(a-x). \tag{2.27a}$$

Designating the relation of constants of monomolecular rate and autocatalytic reaction K_1/K_2 through K, from (2.27a) after integration we obtain

$$\frac{1}{t}\ln\frac{a(K+x)}{K(a-x)}=K_2(a+K)=\text{const.} \tag{2.28}$$

Let us determine time, upon the expiration of which speed of autocatalytic reaction attains maximum. For this expression is differentiated (2.27) by t and the derivative is equated to zero:

$$\frac{d^2x}{dt^2}=[K_2(a-2x)-K_1]\frac{dx}{dt}=0. \tag{2.29}$$

Hence for the maximum rate

$$K_2(a-2x)-K_1=0,$$

or

$$x=\frac{a-K}{2}.$$

Placing this value x in expression (2.28), we obtain an expression for t_{max} – time of achievement of maximum rate:

$$t_{max}=\frac{1}{K_2}\cdot\frac{1}{a+K}\ln\frac{a}{K}. \tag{2.30}$$

Second and third factors as compared to first weakly depend on temperature. Therefore approximately taking their constants and making $K_2 = K_0e^{-E/RT}$, we obtain

$$t=e^{E/RT}\frac{1}{K_0}\frac{1}{a+K}\ln\frac{a}{K}. \tag{2.31}$$

or

$$\ln t = \frac{E}{RT} + B,$$

where

$$B = \ln\left(\frac{1}{K_0}\frac{1}{a+K}\ln\frac{a}{K}\right).$$

Thus, during homogeneous autocatalysis the final products of time logarithm for achievement of maximum speed is linearly related with reverse absolute temperature. The time achievement of maximum speed of transformation can be determined experimentally by its close time delay of self-ignition. Relationship (2.31) permits the dependency of delay of flash on the temperature to approximately determine the activation energy of autocatalytic reaction.

It is necessary to indicate that actual linear dependency between logarithm of flash delay and reverse absolute temperature is not yet the proof that self-ignition has autocatalytic nature.

Known external similarity with autocatalytic flow of process is observed in certain conditions of consecutive reactions taking place. As an example, let us consider the simplest case: transformation of substance A into final product C occurs as a result of two consecutive irreversible monomolecular reactions

$$A \xrightarrow{K_1} B \xrightarrow{K_2} C.$$

Let us assume that initial quantity of substance A equal to a moles, the quantity of reacting substance A to moment of time t equal to x. Then dependency of quantity of unreacting substance on time, will be expressed by relationship of monomolecular reaction

$$a - x = ae^{-K_1 t}. \qquad (2.32)$$

Designating quantity of final product in moment of time t through y, we obtain a quantity of intermediate product at this instant x - y and speed of formation of the final product equal

$$\frac{dy}{dt} = K_2(x-y). \tag{2.33}$$

After integration we obtain

$$y = a\left(1 - \frac{K_2}{K_2-K_1}e^{-K_1t} + \frac{K_1}{K_2-K_1}e^{-K_2t}\right). \tag{2.34}$$

On Fig. 2.9 is shown change in time of quantities of starting substance A (curve 1), intermediate product B (curve 2) and final product C (curve 3).

Quantity of intermediate product, equal in the beginning to zero, is increased in time, passes through a maximum and decreases to zero. Quantity of final product is increased, as during autocatalytic reaction, in the beginning all faster and faster, in conformity with accumulation of intermediate product; in the moment, when quantity of intermediate product passes through maximum, on curve 3 is observed a bend, corresponding to the maximum of speed of formation of final product.

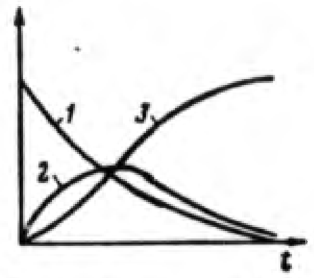

Fig. 2.9. Change of quantities of starting substance (1), intermediate (2) and final (3) products at consecutive reactions.

At definite relationships and absolute values of both constants and induction period can also be observed: rate of formation of final product, the prolonged time remains very small, especially, when process includes several steps.

During formal similarity of consecutive and autocatalytic reactions taking place it is possible to distinguish by various methods, in particular, separating intermediate product and establishing, whether it accelerates the decomposition of starting substance. Absence of acceleration excludes autocatalysis.

4. Chain Autoacceleration of Reaction (Chain Explosion)

General presentations of theory of chain reactions

Theory of chain reactions has its own sources in the works of A. N. Bakha (1897) and N. A. Shilov (1905). Basic development obtained this theory for last decades in the first place in the works of acad. N. N. Semenov and his school, especially in application of gas explosions.

Essence of chain theory consists in the following.

According to the theory Arhenius reaction rate simply is determined by the number of molecules, possessing energy, equal or exceeding activation energy. This number of active molecules is determined by Maxwell-Boltzmann distribution, corresponding to given temperature. However it is necessary to consider that during every elementary reaction energy separated equal E + Q (E – activation energy, Q – heat of reaction). Directly after passage of elementary reaction the energy given off is concentrated in comparatively small number of particles of its products. Such particles during collision with normal molecules, at the expense of their own great energy can activate them or even to enter with them into reaction, which in turn creates new active molecules etc. Thus, actual reaction will create active molecules, where in certain cases their number can become significantly larger than the number of active molecules, appearing as a result Maxwell-Boltzmann distribution of energy. In other words, one primary elementary reaction can create a chain of provoking one another reactions. Length of chain (i.e. number of elementary reactions in it) may be very great. I this case the general speed of reaction will be determined not so much by a number of active molecules, appearing as a result of Maxwell-Boltzmann distribution, but by the conditions of development of chains.

Thus, chain are called such reactions, at which regeneration of active particles takes place.

Essential for chain theory is question about the type of active particles which determines the possibility of appearance of long chains of reaction. In usual conditions of relatively slow activation reactions at the expense of excess kinetic energy of particles cannot give chains of noticeable length, since such energy is rapidly dispersed during collisions. The same pertains to the excitation energy. Conversely, particles, active at the expense of chemical energy (atoms, free radicals), are not able, as a rule, to loose excess energy during collisions with any particle, contained in them in a hidden form, and therefore easily preserve it to the point of encounter with that particle, with which they are able to react.

Reaction product of radical with valence-saturated molecule, inevitably constitutes a radical. Thus, free valence, which a particle possessed, entering into reaction, does not disappear, and is kept in one of the particles of reaction products, i.e. it is regenerated during reaction.

New radical again enters into reaction, leading to the formation of a new radical, usually the same, from which chain began and the reactions cycle is repeated anew.

Disappearance of radicals (beam in chain) can occur due to bonding with each other, accompanied by mutual saturation valency that is possibly only during certain special conditions, characterized usually by much smaller probability than the continuation of chain (these conditions will be considered below).

In virtue of these properties, radicals and free atoms are according to Seed basic type of active particles in chain reactions.

Historically, presentation about chains appeared for explanation of anomalous large quantum yields of certain photochemical reactions. It is known that light energy is absorbed by separate portions — quanta.

Therefore it was naturally expected that the number of molecules, reacting during photochemical reaction, will be equal to the number of absorbed quanta of light, i.e. quantum yield (relation of number of reacting molecules with the number of absorbed quanta) will be equal to unity.

It turned out, however that only in very few cases quantum yield is equal to unit. This occurs because the products of primary reaction enter into secondary reactions. Sometimes these secondary reactions are easy to consider. For instance, in case of photochemical decomposition of hydrogen iodide the quantum yield is equal two. Final products during decomposition of hydrogen iodide are iodine and hydrogen. Absorbing quantum of light of HI molecule breaks up into H and I. Atom of hydrogen reacts with other unexcited molecule of hydrogen iodide

$$H+HJ=H_2+J.$$

Atoms of iodine, being bonded, form a molecule of iodine. Thus, every absorbed quantum evokes decomposition of two molecules.

However for certain photochemical reactions, quantum yield is extraordinarily great, attaining million molecules per quantum. Classical example of such reaction is the photochemical compound of chlorine with hydrogen with a quantum yield near 10^5. For explanation of anomalous large quantum yield, chain diagram of the reaction was offered.

Primary reaction of initiation of chain is the decomposition of a chlorine molecule into atoms during the absorption of quantum of light;

$$Cl_2+h\nu=Cl+Cl. \qquad (a)$$

Atom of chlorine reacts with molecule of hydrogen, forming hydrogen atom and a molecule of HCl:

$$Cl+H_2=HCl+H. \qquad (b)$$

Atom of hydrogen, formed during the reaction (b), reacts with molecule of chlorine, regenerating atom of chlorine etc.

$$H+Cl_2=HCl+Cl. \qquad (c)$$

Thus, formation of one atom of chlorine evokes a whole number of reactions, which is ceased only when as a result of recombination or reaction with impurity will the atom of hydrogen or chlorine disappear.

Different elements of considered chain diagram of a given reaction were confirmed by experiment. Great quantum yield of reaction in the formation of HCl is the corollary of chain mechanism of reaction.

Chain theory permitted to give the correct interpretation and also many cases of positive and especially negative catalysis, when the most insignificant, sometimes immeasurably small quantities of impurities render the strongest influence to the reaction rate. If the positive catalysis is still possible to grasp, assuming that the reacting molecules one after another get on the catalyst, then it is much more difficult to grasp the negative catalysis, when an insignificant impurity of catalyst can almost completely stop the reaction, proceeding in its absence with significant speed. Range of operation of the field force of molecule has an order of its diameter, nonetheless the presence of molecule of negative catalyst affects particles, which are at much large, distances.

As examples it is possible to name the strong lowering of temperature of ignition of many gas mixtures (hydrogen with oxygen, carbon dioxide with oxygen, methane with oxygen and air and others) during the addition of insignificant quantities (0.05%) nitrogen dioxide, opposite influence of impurities of metalorganic compounds, accelerating and braking the influence of different impurities in processes of polymerization and others.

Thus, impurity of oxygen already in quantity of 0.1% strongly inhibits the photochemical reaction of interaction of hydrogen and chlorine. Vapor of iodine, besides at still smaller concentrations strongly inhibits oxidation of hydrogen by oxygen. The same iodine accelerates decomposition of number of organic compounds. Impurity of small quantities of peroxides sharply accelerates oxidation of hydrocarbons. Impurity of azomethane lowers temperature of decomposition of acetaldehyde by 200°. Addition of 1% formic acid lowers the temperature of self-ignition of methaneair mixture from 590 to 320°; the same way act ammonia, ethylhydrogen peroxide, diazomethane and others. Conversely, bromine hydrocarbons, derivatives, and also suspension of certain salts strongly inhibit the beginning and propagation of a flame in a given mixture.

Chain theory explains these phenomena by the following: positive catalyst — this substance, creates initial centers of chain.

For explanation of negative catalysis, it is sufficient to assume that the reaction, whose rate is influenced by catalyst, is a chain reaction. Negative catalyst by one or otherform deactivates one of the particles — participants of chain, preventing all those reactions, which would have a place at the continuation of a given chain. If a chain is very long, then one molecule of negative catalyst can thus decrease the number of reacting molecules by hundreds or thousand.

At last, on the basis of chain theory an explanation was obtained by one more large group of facts, contradicting the Arhenius theory, — phenomenon of upper and lower limits of pressure during self-ignition of many gas mixtures in the region of small pressures.

According to the Arhenius theory, with increase of pressure the gas reaction rate should be monotonously increased. Actually, if one were to admit a gas mixture able to ignite into heated evacuated vessel at very low pressures (millimeters of Hg) and from experiment to increase this pressure, then it is possible to observe phenomenon of limits: at certain pressures it is impossible still to obtain any reaction criteria and at insignificant increase of pressure already is observed self-ignition.

Pressure, at which transition occurs from extremely small speed of reaction to self-ignition, is called lower limit of chain explosion by pressure.

With further increase of pressure higher than known limit a sharp deceleration of reaction is observed, appearing with ceasing of flash. Pressure, at which this occurs, is called upper limit of chain explosion by pressure.

Before crossing to the explanation of phenomena of upper and lower limits, let us stop on conditions of appearance and break of chains, and also their branching.

Appearance of chains, i.e. formation of initial centers of chain, can occur by various ways. Every molecule, obtaining energy, equal or exceeding the activation energy, can start chain of reactions. Activation of molecule can occur at the expense of redistribution of energy during collisions or as a result of action of external agent (for instance, light, electron impact, α-particle and others).

The question about the mechanism of break of chain is more complicated. In above considered chain reaction of hydrogen with chlorine active centers are atoms of H and Cl. One would think, that break in chain is possible by diagram

$$Cl+Cl=Cl_2$$

or

$$H+H=H_2.$$

It is easy to check, however that such recombination of atoms is extraordinarily less probable. So that from molecule were to form two atoms, it should obtain energy, equal or exceeding energy of dissociation. This energy in potential form is contained in the form of free atoms. Let us assume that such atoms met and were bonded into a molecule. It is obvious that energy of vibration of atoms in obtained molecule will be equal or large energy of dissociation. Such molecule cannot exist – it immediately will decompose into atoms.

Bonding of atoms into molecule is possible in the following cases. Let us assume that simultaneously collide two atoms and third (indifferently what kind) particle A. Kinetic energy, which is created at the expense of potential during approach of atoms and hinders their bonding, is transmitted partially to molecule A. In this case atoms cannot part and form a molecule

$$Cl+Cl+A-\overrightarrow{Cl_2}+\overrightarrow{A}.$$

Pointers above Cl_2 and A show that both molecules possess after collision significant growth of kinetic energy, since the heat of association, separating during the reaction, will cross namely into kinetic energy of form molecule and third particle.

The above mentioned pertains to recombination of radicals, at least such, which consist of small number of atoms, for instance CH_3. If radicals consist of large number of atoms, then recombination can occur during double collision, without participation of third particle. In this case excess energy, separated during recombination, is distributed many bonds and turns out to be insufficient, in order to tear one of them.

At low pressures the number of triple impact is very small and the recombination rate of atoms in volume therefore also is small. In these conditions recombination of atoms or radicals occurs on the wall. Solid wall, especially metallic, absorbs very well free atoms and radicals. One may assume that practically all surface of solid body is covered by them. Therefore when atom or radical being in volume, gets on the wall, it usually meets with other atom or radicals, absorbed on the surface, and easily reacts with him, since any of the nearest molecule of substance of wall can play role of third particle A. Thus, break in the chain occurs on wall or at the triple collision in volume.

Dependence of speed of chain reaction on time

Chain reaction in which take place only two processes – the continuation and break in chains – is distinguished from unchain reaction in two respects. First, speed of chain reaction (number of molecules, reacting in unit of time) is larger than it corresponds to the number of active particles, appearing in unit of time according to Maxwell-Boltzman, since every active particle evokes chain of reactions. Secondly, speed of reaction in initial stage is increased in time, rushing to its own maximum value. In the initial moment of time the reaction rate is determined, obviously, number of forming according to Maxwell-Boltzman of active particles; by measure of its development of chains number i.e. speed of reaction, rapidly increases and attains a constant value; besides the number of broken chains becomes equal to the number of appearing chains.

However, during chain processes can occur not only reaction of continuation of chain, at which formed as any active particles, as many of them enters into reaction, and reaction of break, at which active centers are turned into stable molecules. Branching of chain can also take place, when reaction, which one active particle enters, leads to the formation of large number of active particles, i.e. one chain on certain section gives the beginning of new chains.

At the expense of this branching, if it obtains significant development, it can absolutely change the character of reaction; from reaction of usual type with speed, incident in time due to decrease of concentrations of reagents, it becomes self-accelerated. This occurs then, when branching is so significant that it not only compensates break in chains and decrease of concentration of reagents, but also leads to continuous increase of number of active particles. For the simplest case, when we do not consider change of concentrations of initial reagents with respect to time, the shown condition is fulfilled, if branching occurs more frequently than break in chain. In that case the number of appearing active particles in any moment of time will be larger than the disappearing number due to break, and therefore the number of chains, i.e. reaction rate will be continuously growing. This is the condition of beginning of chain explosion (flash).

Let us write in general the expression for change of concentration of leading active particles, determining the rate of the slowest link of chain process, and consequently also all process on the whole, in the following form:

$$\frac{dn}{dt}=w_0+(f-g)n, \qquad (2.35)$$

where n — concentration of leading active particles;

f and g — kinetic coefficients* reactions of branching and break of chains (relation of rate of corresponding reactions to concentration of leading radical);

---

*If reaction of branching and break occur according to diagram

$$n + M_1 \rightarrow$$

and

$$n + M_2 \rightarrow$$

w_0 – concentration of the active particles, forming in unit of time at the expense of Maxwell-Boltzman distribution of energy.

Integrating and assuming that n = 0 at t = 0, we obtain

$$n = \frac{w_0}{g-f}\left(1 - e^{(f-g)t}\right). \tag{2.36}$$

Reaction rate w is equal to product of kinetic coefficient a, characterizing the reaction of continuation of chain, on concentration n of active centers:

$$w = an.$$

When f < g, i.e. branchings is significantly less than break, then at small values t last member of expression (2.36) can be disregarded to write

$$n = \frac{w_0}{g-f} \tag{2.37}$$

and

$$w = \frac{aw_0}{g-f}.$$

Change of reaction rate in time in case f < g corresponds to curve 1 on Fig. 2.10.

If f = g, then

$$dn/dt = w_0,$$

whence

$$n = w_0t. \tag{2.38}$$

[FOOTNOTE CONT'D FROM PRECEDING PAGE].
(here n – leading radical; M_1 and M_2 – other participants of reaction) and constant of speed of these reactions corresponding to K_1 and K_2, then $f = K_1[M_1]$ and $g = K_2[M_2]$.

Reaction rate $w = an = aw_0t$ will be linearly increased in time (Fig. 2.10, curve 2).

If $f > g$, then integral of equation (2.35) has the form

$$n = \frac{w_0}{f-g}\left(e^{(f-g)t} - 1\right), \tag{2.39}$$

and reaction rate

$$w = \frac{aw_0}{f-g}\left(e^{(f-g)t} - 1\right), \tag{2.40}$$

or, for not too small t, when $e^{(f-g)t} \gg 1$,

$$w = Ae^{\varphi t}, \tag{2.41}$$

where

$$A = \frac{aw_0}{f-g};$$
$$\varphi = f - g.$$

Thus, if $f > g$, then speed of process without limit is increased in time by model law (Fig. 2.10, curve 3). Besides the more difference $f - g$, the faster is speed increased. Condition $f \geq g$ constitutes condition of appearance of chain explosion.

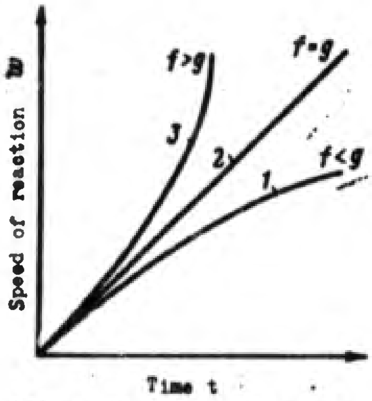

Fig. 2.10. Change of speed of chain reaction in time.

From equation (2.41) formally it follows that at $t \to \infty$ the reaction rate becomes infinite; physically this, of course, is not so: along with increase of concentration of active particles rapidly decreases the source of these particles – starting substances. Increase of reaction rate is delayed, it passes through maximum with subsequent lowering. However maximum may be very great and can correspond to the passage of practically all reaction in small shares of second that we call it chain explosion.

Boundary between the chain reaction with terminal velocity and chain explosion is, as one may see, equality of speeds, branching and break of chains. When the speed of active particles appearance becomes larger than the speed of break of chains, a transition is observed from slow chain reaction to flash.

Explanation of lower and upper limits chain reaction by pressure

Phenomenon of limits will be considered on the example of mixture of hydrogen and oxygen.

On Fig. 2.11 is shown change of speed of reaction w depending upon pressure. Here p_1 – lower limit of chain explosion by pressure, p_2 – upper limit. Chain explosion is observed in shaded region of pressure between p_1 and p_2.

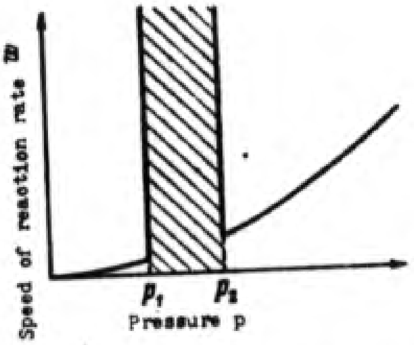

Fig. 2.11. Dependency of speed of interaction of hydrogen with oxygen from pressure.

Absence of reaction at pressure below p_1 is explained by the following.

Length of chain at small pressures is small because the probability of break is great, which in given conditions occurs practically only on the wall, since in volume the number of triple collisions as compared to number of double will be insignificantly small. At small pressures the length of free path is great and chain, appearing in volume, rapidly, through several sections, gets on the wall, where it is broken. If speed of appearance of initial centers is small, then at short chains the speed of reaction may be so low that its impossible to reveal by usual methods.

By measure of increase of pressure the speed of break of chains on wall decreases or remains constant, but speed of branching of chains increases proportionally to pressure. Therefore effective length of chain is increased at first very slowly, and then, as experiment show calculation is extraordinarily sharply. It is sufficient to change the pressure on shares of millimeter of Hg, so that practically inconspicuous reaction beginning to flow with very great speed and received character of explosion.

Correctness of considered explanation below the limit p_1 it is possible to check by following ways.

1. The larger the diameter of vessel, the subjects more difficult than chain to get on wall and flash in vessel of large diameter should be possible during smaller pressure, i.e. lower limit will be lowered with increase of diameter of vessel. Such influence of diameter of vessel is observed in reality.
2. If at constant diameter of vessel an inert gas is added in this, then the hit of chain on wall is hampered and at known conditions of chain length increases. A paradoxical phenomenon can be obtained: the admission of inert gas in vessel with mixture of gases, able to chain reaction, interaction rate of which at a temperature and pressure $(p < p_1)$ experiment is practically equal to zero, will be called flash. In other words, presence of inert gas will lower the lower limit (in this case under lower limit is implied partial pressure of mixture of reacting gases); besides influence of inert gas will be more even greater than less its diffusion, coefficient, i.e. the more molecular weight. Such influence of inert gases is confirmed by experiment.
3. Magnitude of lower limit strongly depends on material and state of walls of vessel. This is explained by the fact that different materials in various degrees are able to break chain. Thus wall from metal or graphite break the chain at every hit on them by atom of hydrogen. Conversely, for glass walls the probability

of break at hit of chain on wall very is small, but strongly increases during washing of vessel of solution of potassium chloride.

Role of material of wall at break of chains graphically is illustrated by following experiment of Nalbandyan. If in glass vessel with mixture of hydrogen and oxygen at 440°C (lower limit in these conditions 0.94 mm) is inserted a thin metallic rod, then lower limit is increased to 7 mm. At fast pulling of rod it is possible to observe intense flash, accompanied by burning out of mixture to limit, responding glass vessel without rod.

Let us note that wall sometimes can execute function of not only break of chains, but also their initiation.

Upper limit is in agreement with Semenov is determined by the following mechanism.

With increase of pressure the number of triple collisions, leading to break of chain in volume, which is proportional to the cube of pressure, increases stronger than number of double collisions, proportional to square of pressure. At pressure, corresponding to upper limit, reaction rate of break of chains becomes larger than the reaction rate of branching. As a result at pressures with larger p_2 self-ignition does not occur.

This explanation is in accordance with following experimental data:

1) upper limit does not depend on diameter of vessel;
2) impurity of inert gas lowers upper limit;
3) from state of walls and its accidental changes of the upper is limiting in contrast to lower, does not depend.

Along with pressure on appearance of ignition influences temperature. On Fig. 2.12 in coordinates pressure – temperature are given experimental data for mixture of hydrogen with oxygen. On the right from curve ABCD is the region of ignition, on the left – slow reaction. AB – is lower limiting BC – upper limit. At

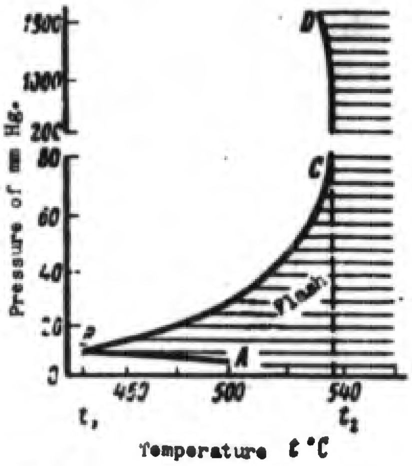

Fig. 2.12. Regions of slow reaction and self-ignition of hydrogen oxygen mixture.

temperatures lower than t_1 ignition is not observed. Higher than t_1 ignition takes place, where interval of pressure between upper and lower limit the wider than above temperature. When temperature exceeds t_2, upper limit is not observed. Influence of temperature is determined by the fact that its increase increases speed of reaction of branching of chains and besides to a larger degree than speed of reaction of break.

Mechanism of chain reaction between hydrogen and oxygen

For concretization of above-stated general presentations of chain theory, we consider chemical mechanism of interaction of hydrogen with oxygen, taking place under certain conditions as entirely branched chain.

On the basis of works of Semenov, Kondrat'ev, Voivode, Nalbandyan and others for this reaction is taken following mechamism: inside flash region reaction should follow the mechanism of branched chains. General diagram of such process has the form

$$X + A = Y + Z,$$

where X, Y, Z — active centers of reaction;

A — molecule of parent substance (H_2 or O_2).

With this process complete processes of break chains and thus braking development of reaction.

Totality of elementary reactions has following form:

$$\left.\begin{array}{l} \text{I. } H_2 + O_2 = 2OH \\ \text{II. } H_2 + M = 2H + M \\ \text{III. } O_2 + O_2 = O + O_3 \end{array}\right\} \text{ onset of chain.}$$

Here M — any molecule.

$\text{IV. } OH + H_2 = H_2O + H$ continuation of chain.

$\left.\begin{array}{l} \text{V. } H + O_2 = OH + O \\ \text{VI. } O + H_2 = OH + H \end{array}\right\}$ branching of chain.

$\left.\begin{array}{l} \text{VII. } H \xrightarrow{\text{wall}} = {}^1/_2 H_2 \\ \text{VIII. } OH \xrightarrow{\text{wall}} = {}^1/_2 H_2O_2 \end{array}\right\}$ break of chain on the wall.

$\text{IX. } H + O_2 + M = HO_2 + \vec{M}$ break of chain in the volume.

With subsequent reactions

$$\text{X. } HO_2 \xrightarrow{\text{wall}} \left\{\begin{array}{l} {}^1/_2 H_2O_2 + {}^1/_2 O_2. \\ {}^1/_2 H_2O + {}^3/_4 O_2. \end{array}\right.$$

$\left.\begin{array}{l} \text{XI. } HO_2 + H_2 = H_2O_2 + H \\ \text{XII. } HO_2 + H_2 = H_2O + OH \end{array}\right\}$ continuation of chain through little-active radical HO_2.

During ignition and burning in region between lower and upper limit the basic role plays the reaction of branching of chain V and VI. Break in chain goes mainly on the wall by reaction VII.

With increase of pressure the number of triple collisions increases, leading to break of chain by reaction IX with the formation of little-active radical HO_2, which is decomposed on the wall by reactions X.

Indirect proof of correctness of considered mechanism is the coincidence of obtained theoretical regularities on limits of ignition and dependencies of induction period (influence of dimensions of vessel, material of walls, composition of mixture, impurities of inert gases and others) with experimental data. For slow oxidation at pressures higher than upper limit value of separate reactions is already different than in flame.

Role of reaction V, proceeding through double collisions, decreases as compared to reaction IX. Concentration of atomic hydrogen decreases because reaction VI becomes relatively rare. Branchings of chain starts to play a secondary role, and a slow reaction instead of ignition occurs. Increase of general pressure hampers the diffusion and destruction of the radical HO_2 on wall, which now can react in a volume, in particular, by reaction XI (formation of hydrogen peroxide during slow oxidation of hydrogen in this region of pressures).

Concentration of hydroxyl in zone of slow reaction also is much lower than in rarefied flames. Leading at sufficiently large pressures (higher than the upper limit) become the sequence of reactions IX, XI and X.

Thus, the same totality of elementary reactions determines the mechanism and slow oxidation and ignition, but the role of separate reactions in these two processes essentially is changed.

Direct proof of considered mechanism of slow oxidation and burning of hydrogen was the direct detection of hypothetical intermediate substances and determination of their concentration.

V. N. Kondratev and his pupils with the help of special spectroscopic methods the absolute concentration of hydroxyl in rarefied hydrogen-oxygen flames was measured. This concentration turned out to be in thousand times more concentration of hydroxyl, which could be established at a temperature and pressure of flame at the expense of equilibrium

$$H_2O \rightleftarrows H + OH.$$

Thus was established a chemical (and not thermal) origin of hydroxyl in flame and its active role in mechanism of oxidation of hydrogen.

On the basis of accepted mechanism of process it is possible to calculate also the concentration of atomic hydrogen. Such calculations give partial pressure of atoms in the order of 10% from general pressure. Such high concentrations of H atoms facilitate the problem of its direct detection. However in distinction from the hydroxyl spectroscopic method was inapplicable, since the line of absorption of H atoms are covered by intense absorption band of steam.

Kondratev and Kondrateva resolved this problem by thermoelectric method. In the zone of hydrogen flame were introduced two thin thermocouples, protected from direct influence of flame by thin-walled quartz tubes. Tip of protective tube of one of thermocouples was covered with $ZnOCr_2O_3$, protective tube of second thermocouple is washed with hot nitric acid. Surface, covered with $ZnOCr_2O_3$, turns out to be extraordinarily effective with respect to recombination of H atoms. The heat given off heats the thermocouple that does not have place for control thermocouple since the quartz surface washed by nitric acid, with respect to ~~recombination~~ is effective very little. Therefore in presence of atoms H between both thermocouples is established definite difference of temperature ΔT, whom magnitude depends on concentration of atoms. Results of determination of this concentration well will agree with theoretical calculation.

Chain reactions with degenerated branchings

(Chain-heat initiation of explosion)

Speed of branched chain reaction according to (2.41) is exponentially increased in time.

Calculation shows that rate increase at usual branching, combined with reactions of free radicals, should occur comparatively fast. Reactions are known, for instance for oxidation of many hydrocarbons, the rate of which increases according to the law (2.41), but very slowly, during minutes, hours and even days. For explanation of such delayed development of reaction Semenov permits the existence of chains with "degenerated branchings."

Development of chain in this case is accompanied by formation of comparatively stable molecular intermediate product. During transformation of this product, radicals are formed, i.e. branching of chain occurs. However the speed of transformation much less than the speed, with which the products of radical type enter into reaction, and therefore φ is small. Branching occurs, as a rule, a significant time after the chain reaction, producing molecular intermediate products, was developed and break occurred.

As an example of chain reaction with degenerated branchings it is possible to use oxidation of methane, which plays an important role in the processes of ignition of gas in mines (see Chap. X).

In agreement with Semonov it proceeds by the following. At relatively high temperatures as primary product, determining the degenerated branching, is, apparently, formaldehyde, reacting according to equation

$$HCHO+O_2 \rightarrow HCO+HO_2-32 \text{ kcal}$$

As the activation energy of this reaction it is possible approximately to take it equal to its thermal effect.

Reaction of primary onset of free radicals from parent substances, for instance

$$CH_4+O_2 \rightarrow CH_3+HO_2-55 \text{ kcal},$$

occurs significantly more difficulty.

In beginning of reaction, when aldehydes are still few, speed of reaction of onset will be

$$w_{CH_4}=K_0[CH_4][O_2] \approx 10^{-10} e^{-\frac{55\,000}{RT}}[CH_4][O_2].$$

By measure of accumulation of aldehydes, radicals will start to be engendered by reaction

$$HCHO+O_2 \rightarrow HCO+HO_2-32 \text{ kcal}$$

with speed

$$w_{HCHO}=K_r[HCHO][O_2] \approx 10^{-10} e^{-\frac{32\,000}{RT}}[HCHO][O_2].$$

Designating by α relation

$$\frac{w_{HCHO}}{w_{CH_4}}=\frac{K_r[HCHO][O_2]}{K_0[CH_4][O_2]}=e^{\frac{23\,000}{RT}}\frac{[HCHO]}{[CH_4]},$$

will find that at T = 700°K

$$a = 10^{7.15}\frac{[HCHO]}{[CH_4]}.$$

This means that in initial mixture of methane with oxygen speed of onset of primary radicals at 423°C will be in 14,000 times less than in this mixture; containing 0.1% HCHO.

Thus, by measure of reaction occurrence and accumulation of aldehyde speed of process, in the beginning frequently is immeasurably small, it is self-accelerated due to development of reaction $HCHO + O_2 \rightarrow HCO + HO_2$ - 32 kilocalories which determines the observed period of induction, typical for chain reactions with degenerated branchings.

Reactions of development of chain of oxidation of methane initial stage at temperatures higher than 300-350°C can be represented by following diagram:

a) $CH_4 + O_2 \rightarrow CH_3 + HO_2$ onset of chain;

$$\left.\begin{array}{ll} b) & CH_3 + O_2 \rightarrow CH_2O + OH \\ c) & OH + CH_4 \rightarrow CH_3 + H_2O \end{array}\right\}\text{ continuation of chain;}$$

$$\left.\begin{array}{ll} d) & CH_2O + O_2 \rightarrow HCO + HO_2 \\ e) & HCO + O_2 \rightarrow CO + HO_2 \\ f) & HO_2 + CH_4 \rightarrow H_2O_2 + CH_3 \end{array}\right\}\text{ degenerated branching;}$$

$$\left.\begin{array}{ll} g) & OH \xrightarrow{\text{wall}} \\ h) & CH_2O \xrightarrow{\text{wall}} \end{array}\right\}\text{ break in chain.}$$

Last reaction considers the possibility of heterogeneous oxidation of formaldehyde on walls of vessel.

Given diagram does not consider reaction between leading chain by radicals and aldehyde (for instance, $OH + CH_2O \rightarrow H_2O + HCO$). This position justly only for the most initial phase of transformat ion. By measure of accumulation in the course of transformation of aldehyde these reactions start to play more essential role, and, if one were to consider the further movement of transformation, then the above mentioned diagram of oxidation of methane it is necessary to supplement by reactions of radical OH with aldehyde, and also reactions HCO and HO_2.

Development of chain during degenerated branchings can pass very slowly. Dependency of speed of reaction from time is depicted (at constant temperature) curve, having maximum (Fig. 2.13), time of achievement and absolute value of which depend on a number of conditions. Reaction goes by, self-acceleration, but due to slowness of development of chain, the maximum rate begins then, when parent substance already in larger or smaller degree has been exhausted; as a result the maximum turns out to be relatively low.

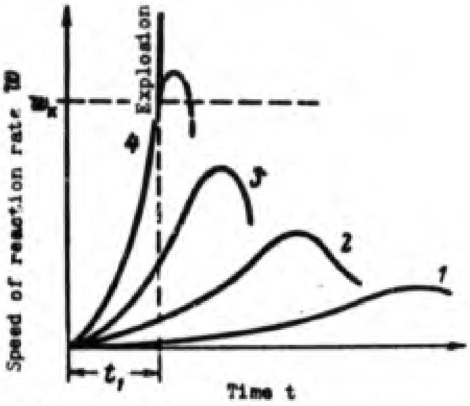

Fig. 2.13. Chain-heat explosion according to Semenov.

Let us assume, however, that during development of reaction, its rate will attain such value, at which heat gain becomes larger than radiation heat. Then on slow isothermal acceleration of chain reaction a fast thermal acceleration is accumulated. Combination of both mechanisms of acceleration in certain conditions of temperature and heat loss can lead to appearance of <u>chain-heat explosion</u> (curve 4). Chain processes of types, depicted by curves 1, 2, and 3, are called by Semenov, as <u>degenerated explosions.</u>

Condition of explosion can be formulated as achievement of certain critical for given conditions of experiment of reaction rate corresponding to exceeding heat gain above heat loss:

$$w = Ae^{\varphi t} = w_{\text{к}} = \text{const},$$

or approximately

$$\varphi\tau = \text{const}, \tag{2.42}$$

where τ — time from admission of gas into vessel to initiation of explosion.

Since

$$\varphi = Ce^{-E/RT},$$

then

$$Ce^{-E/RT}\tau = \text{const}$$

and

$$\tau = \frac{\text{const}}{C}e^{E/RT},$$

or

$$\tau = Be^{E/RT},$$

whence

$$\ln\tau = \frac{E}{R}\frac{1}{T} + \ln B. \tag{2.43}$$

Thus, during chain-heat explosion logarithm of time of delay of explosion is linearly related to the reverse absolute temperature. This relationship allows to establish activation energy of reaction of transformation of intermediate product, determining development of chains with degenerated branchings.

Chain reactions during decomposition of solid compounds

In a number of cases self-accelerated decomposition of solid matters follows regularities of chain reactions with degenerated branchings. Decomposition is accelerated in time according to the law $w = Ae^{\varphi t}$; besides rate increase at moderate temperatures goes slowly enough i.e. φ is small. An induction period is observed and delay of flash, whose magnitudes are changed with temperature in accordance with chain theory.

In agreement with Semenov, such transformations in the solid phase represents indeed the chain reactions with degenerated branchings, where intermediate products possess significant stability at room temperature.

Initial centers of reaction appear usually on surface of crystal, rarer – in volume and, by reacting, create an intermediate products, less stable than initial molecule. These products are turned into final products of reaction, and with this transformation the neighboring molecules of unreacted substance are activated that leads to their transition into intermediate products etc. As a result of repetition of this sequence of reactions from one active center starts to grow in thickness the crystal thread of reaction. Now and then intermediate product evokes decomposition of two neighboring molecules and then from basic thread begins to grow a side thread – branching of chain occurs. Thus, reaction is developed in the form of incorrect "tree," branch of which root in thickness of crystal.

If one were to interrupt the reaction, by cooling the vessel, and then continue it anew, then reaction will proceed with the same speed, as if interruption did not take place. This fact shows that intermediate product is sufficiently stable at room temperature.

By measure of a tree growth the reaction with large space inside a crystal occupies the thread of particles of the final reaction product, thus it becomes already a layer of unreacting substance. Space, in which the chains are developed narrows. If final product breaks the chain, then branching occurs relatively rarer and, at last, chain in large number begin to be broken rather than branched, φ from positive becomes negative and reaction rate, passing through maximum, starts to drop.

It is necessary to indicate that fulfillment of exponential law of increase of reaction rate with respect to time is possibly not only during chain processes. Such law will be observed in all cases, when reaction rate by this or other causes turns out to be proportional to the quantity of reacting substance.

Thus, Garner for explanation of the shown law initially took, the proceeding from presentations of Smexal on the structure of crystals,* that seeds of reaction appear in separate crystallites and can pass from them to the neighboring crystallites by bridges of amorphous substance.

Other explanation of this law was advanced by Prout and Thompkins. These authors assume that initially as a result of reaction on the crystal surfaces accumulation of molecules of product will be formed, which creates lateral stresses, leading to formation of cracks. At the mouth of this crack reaction occurs easier and by the

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*According to hypothesis of Smexal, crystals have mosaic structure. Ultramicroscopic cracks divide crystal into very little separate crystallites, cemented by amorphous substance.

walls penetrates inside the crack. Formed at the walls of crack, accumulation of molecules of products leads to the formation of new cracks, proceeding normally to the surface of the first etc. By measure of process development, the branching of cracks is delayed, since they all more and more frequently meet with the surfaces, where substance already reacted, and the reaction rate, passing through maximum, starts to drop.

Equation, developed by Prout and Thompkins for the described process, analogous to usual equation of chain reaction, but considers not only probability of branching, but probability of break of chains, which is taken to increase proportionally x/x_1, where x_1 — quantity of reacting substance in moment of maximum of speed. For decomposition of number of solid matters ($KMnO_4$, $AgMnO_4$, PbC_2O_4, NH_4ClO_4, and others) this equation is fulfilled for large share of passage of reaction rather than simple exponential dependency. Presentations of Prout and Thompkins will agree that at thermal decomposition (and also during burning) many solid ES is observed cracking of crystals into parts.

Topochemical reactions during decomposition of solid substances

If chain reaction in the solid phase is characterized by great speed of branching of chain, then mathematical regularities of its flow take somewhat unusual form. In this case the active center already on early stages of process evokes reaction of all adjacent to it molecules of substance. Then reaction spreads no longer in the form of branchy tree, but in solid front, behind which all substance reacted.

In most cases of transformation three stages are included: 1) initial reaction, occurring on surface of crystals with yield of gases, 2) formation of seed of new phase and 3) reaction, flowing on interface phases.

Starting on surface of crystals reaction can flow differently: it may be limited by surface layer or spreads by diffusion inside crystal. Activation energy of this reaction, as a rule, is larger than activation energy of subsequent reaction of growth of seeds (for barium azide for instance, value E constitute accordingly 37 and 23 kilocalories/mole). Seeds, forming as a result of surface reaction, usually are three-dimensional, and their surface grows proportionally to the square of time. It is necessary to note that in initial, period of growth seeds of new phase can grow slower, or also faster than subsequently, when linear speed of their growth becomes constant.

Question on seed initiation and development at the early stages of its own existence, is not fully clarified. In certain cases appearance of seeds is caused by surface reaction, forming vacancies in crystal grid of usually anionic character. These moles can be motionless, or also possess mobility on surface or penetrate inside crystal. Aggregation of these moles, when it attains definite dimensions, becomes unstable and leads to formation of seed of new phase; if their number is not too great, then through certain time it is possible to observe the formation of macroscopic discrete seed of reaction. Besides reaction flows practically wholly on surface of contact of its products with parent substance. Regularities of transformation in this case is the same, as during reaction, taking place in solid phase and catalyzed by final products.

If parent substance and catalyst are gaseous or liquid, then the last one is distributed evenly in the whole volume and speed of catalytical reaction is proportional to its quantity (in the simplest case in the first degree). If however the catalyst and parent substance are in solid state, then contact between them is possible only on interface of motionless particles of products of reaction and unreacting substance; in this case speed of catalytical reaction is changed proportionally magnitude of this surface. Such reactions are called topochemical.

During topochemical reactions decomposition starts usually on surface of crystal, in separate points of which appear seeds from products of reaction; once formed, these seeds rapidly root inside the crystal. Reaction rate is determined, thus, by the rates of two processes: 1) formation of seeds and 2) their growth.

Calculation of simultaneous flow of these processes leads to complicated dependency of reaction rate on time. Much simpler regularities are obtained in particular cases, when the rate of process of formation of new seed can be considered practically equal to zero, or be very large. The last one is observed, when energy of activation of surface reaction, leading to formation of seeds and energy of activation reaction of their growth are close. These cases will be considered.

Regularities of topochemical reaction in the case, when speed of formation of seeds practically is equal to zero

In this case the number of seeds can be considered constants and the speed of reaction is determined by speed of seed growth which is proportional to their surface.

For one seed it is possible to write

$$\frac{dx}{dt}=K_1S, \tag{2.44}$$

where S — part of surface of seed, being in contact with undecomposed substance;

K$_1$ — constant of reaction rate.

If one were to consider that seed, appearing on flat surface of the crystal (Fig. 2.14a), has the form of a hemisphere, then S = $2\pi r^2$, where r — radius of seed. If weight of reacting substance, forming the seed, is designated by x, and density of products of reaction through d, then volume of seed

$$\frac{x}{d}=\frac{2}{3}\pi r^3,$$

whence

$$r=\left(\frac{3}{2\pi d}\right)^{\frac{1}{3}}x^{\frac{1}{3}}. \tag{2.45}$$

Putting (2.45) in (2.44), we obtain

$$\frac{dx}{dt}=K_1 2\pi\left(\frac{3}{2\pi d}\right)^{\frac{2}{3}}x^{\frac{2}{3}},$$

or

$$\frac{dx}{dt}=Kx^{\frac{2}{3}}, \tag{2.46}$$

where

$$K=K_1 2\pi\left(\frac{3}{2\pi d}\right)^{\frac{2}{3}}.$$

Integration gives

$$3x^{\frac{1}{3}}=Kt+\mathrm{const.} \tag{2.47}$$

If x = 0 at t = 0, then equation will take the following simple form:

$$x = K_2 t^3, \qquad (2.47a)$$

where

$$K_2 = \left(\frac{K}{3}\right)^3.$$

Differentiating (2.47a) by t, we obtain the rate as a function of time

$$\frac{dx}{dt} = K_3 t^2, \qquad (2.48)$$

where $K_3 = 3K_2$.

If not one but n is obviously simultaneously appearing seeds, then it is obvious that the reaction rate and quantity of reacting substance as function of time will be expressed by the same formulas, but constant will be in n times more.

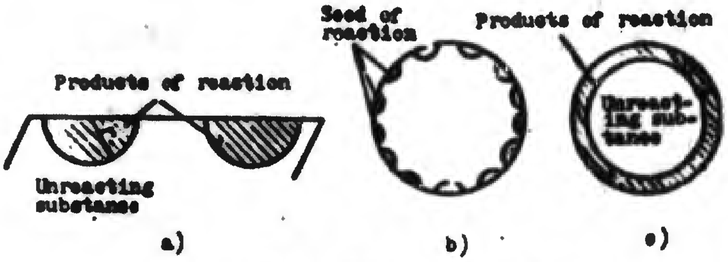

Fig. 2.14. Diagram of development of topochemical transformation.

It is clear that fixed regularities will be executed only as long as separate seeds will not touch each other, after which the reaction rate will be increased slower and at last will start to drop.

Regularities of topochemical reaction in case, when rate of formation of seeds is very great

In this case seeds rapidly cover the surface of crystal (Fig. 2.14b), which quickly turns out to be as if in shell from products of reaction (Fig. 2.14c). Reaction rate is proportional to the surface of undecomposed part of crystal. If one were to allow that crystal has a form of sphere and quantity of undecomposed substance is designated by (a - x), then it is possible to show that the reaction rate will be proportional to the quantity of undecomposed substance by order of 2/3:

$$\frac{dx}{dt} = K(a - x)^{\frac{2}{3}}. \qquad (2.49)$$

After integration, placing t = 0 and x = 0, we obtain

$$a^{\frac{1}{3}} - (a - x)^{\frac{1}{3}} = \frac{1}{3}Kt. \qquad (2.50)$$

Topochemical reactions as a particular case of chain reactions

Comparing mathematical regularities of chain and topochemical reactions (for case, when developed seeds do not hinder each other), it is not difficult to ascertain their similarity.

If speed of reaction of branching and number of chains are small, then the chain reaction rate is proportional, as it is easy to show, to the first degree of quantity of reacting substance:

$$\frac{dx}{dt} = K_1 x. \qquad (2.51)$$

For dependency of speed of reaction on time we have

$$\frac{dx}{dt} = K_2 e^{\varphi t}. \qquad (2.52)$$

If speed of reaction of branching is large, that the decomposition of molecule evokes decomposition of all adjacent to it molecules, then separate threads of reactions, merging, form solid spherical front and speed of reaction increases by topochemical law

$$\frac{dx}{dt} = K_9 x^{2/3} \tag{2.53}$$

—meaning of which consists in that that with respect to possibility of continuation and branching of chains are effective only particle of products of reactions, which are on the surface of seed. Dependency of reaction rate with respect to time is expressed, as was shown, by relationship (2.48)

$$\frac{dx}{dt} = K_9 t^n.$$

In intermediate cases exponent at x in (2.53) is changed from 2/3 to 1 and correspondingly index at t in expression (2.48) is changed from 2 to large values.

§ 4. Slow Chemical Transformation of Condensed Explosives

1. The General Characteristic of Slow Chemical Transformation of Explosives

The application of the considered basic laws of chemical kinetics and slow chemical transformation of liquid and solid explosives, occurring at temperatures lower than the detonation temperature, is hampered by the complexity of reactions flowing in this case. As a rule, chemical transformation of explosives includes not one, but several consecutive or in parallel proceeding reactions, where, depending on conditions, the role of each of them may be different.

On page 42 several equations were given according to which the decomposition of ammonium nitrate proceeds at various temperatures.

A similar change of the composition of products of decomposition with a change of temperature is established for thermal disintegration of nitroglycerine and nitrocellulose (Table 2.3).

Table 2.3. Composition (in Percent by Volume) of Gaseous Products of the Disintegration (Without Water) of Nitroglycerine and Nitrocellulose at Different Temperatures

Decomposing substance	Temperature of decomposition in °C	Products of disintegration in % by volume				Volume of gases cm³/g	Loss in weight at end of experiment, in %
		CO_2	CO	NO	N_2+N_2O		
Nitroglycerine	85—90	34	6	52	8	—	—
	165	30	22	37	11	—	—
Nitrocellulose	120	30,2	17,4	21,4	31,0	156,5	48,6
	145	35,7	16,8	29,6	18,5	200	86

From Table 2.3 it is clear that for both explosives with the change of temperature of the experiment the content of the separate gases is strongly changed. For nitrocellulose the loss in weight and volume of the formed gases was also measured. With an increase of temperature, the loss in weight and volume of the gases are increased, which indicates a deeper transformation of the parent substance.

Even such simple compounds, as azides, at various temperatures give different products of disintegration, calcium axide (CaN_6), for instance, at low temperatures (100-150°C) is turned into a substance, corresponding to the empirical formula $(CaN)_n$, while at detonation the nitride (Ca_3N_2) and metal are formed.

For many explosives various products of disintegration are obtained not only at different temperatures; the composition of products can also be changed in the course of one and the same experiment, conducted at a constant temperature.

According to Capozhnikov, the content of compounds of nitrogen (in gram-atoms) in gaseous products of the initial stage of decomposition of nitrocellulose at temperatures close to the detonation temperature exceeds content of carbon compounds 6.5 times, at the end of the experiment the content of nitrogen is only 1.5 times greater than the carbon content.

In the beginning of decomposition of certain liquid nitroesters (nitroglycerine, nitroglycol, methylnitrate) in an empty and sealed tube at different temperatures from 70 to 240°C, the gas phase turns strong brown as a result of the formation of nitrogen peroxide. Then the intensity of the color of the gases decreases and at the end of experiment they become colorless, analysis reveals a significant content nitrogen oxide in addition. It is natural to assume that the discoloration of gases occurs as a result of oxidation by nitrogen peroxide of organic products of initial stages of disintegration, but possibly, also the initial nitroesters.

Thus, even with a constant temperature of the experiment disintegration of explosives is a complicated series reactions. With a change of temperature the proportion of separate reactions can be changed essentially, but sometimes the character of the expression of disintegration as well, which complicates the picture even more.

In spite of this, in the complicated complex of consecutive and parallel reactions of slow chemical transformation of explosives, it is possible to distinguish two types of processes. Experience shows thermal disintegration of explosives starts by a primary reaction, flowing for the substances studied in this respect according to the law of reaction of the first order. A primary reaction is the slowest of possible reactions of the disintegration of a given explosive. The speed of primary reaction depends only on the nature of the substance, its aggregate state and temperature. Kinetic characteristics (energy activation E, pre-exponential factor B) of the primary reaction for a number of explosives are given in Table 2.5 on page 149.

By means of the accumulation of products of a primary reaction secondary, usually self-accelerated, reactions are developed. The nature and magnitude of the speed can be different and depends on the conditions of the flow of the transformation. Speed can be evoked by the products of disintegration, intermediate or final, as a result of their catalytic action, and also by the reaction of these products with each other or with an undecomposed substance. The speed of formation of the final product can be increased also in the case when the transformation goes by the type of consecutive reactions.*

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*The flow of the transformation is like a number of consecutive

The speed of the primary reaction usually is relatively small and decreases in time in conformity with a decrease of the quantity of the unreacting substance. This speed can also increase in time, but only in the case when the primary reaction goes with liberation of heat, and heat withdrawal is prevented and the temperature of the explosive does not remain constant.

Conversely, the development of the self-speed of secondary reactions is not caused by the necessity of self-heating and the speed of them increases even in the case when the temperature remains constant. In the beginning, the speed is small, since causes for speed are lacking, but then in time it increases more or less rapidly. If the speed of secondary reactions goes faster than the drop of speed of the primary reaction, then the total speed of transformation of the explosive is increased. Therefore in many cases, the thermal disintegration of an explosive is self-accelerated process.

In the cases when the speed of the total exothermic reaction is great, its speed can attain such large values that equilibrium between incoming heat and heat withdrawal is disturbed and thermal self-ignition occurs. Such is the usual mechanism of the detonation of an explosive, which appears with heating after a certain (sometimes prolonged) time.

This general picture of the flow of the process will be explained on the example of disintegration of nitroesters, nitro compounds and certain explosives, which disintegrate in the solid state.

[FOOTNOTE CONT'D FROM PRECEDING PAGE]
reactions especially in the case of explosives containing several identical groups, from which disintegration of the molecule is started – polynitrate compounds and so forth. It is natural that the primary process in this case is the reaction of one group, which does not necessarily immediately lead to complete disintegration of the molecule.

2. Slow Chemical Transformation of Nitroesters

The decomposition of nitroesters with a low boiling point (methylnitrate 66.5°, ethylnitrate 87°) was studied only in vapors; with higher boiling nitroesters (nitroglycol 200° nitroglycerine 245°) research was conducted on vapors, as well as in the liquid state. The decomposition of cellulose nitrates was investigated in solid state.

The disintegration of a simple ester of nitric acid — methylnitrate (CH_3ONO_2) apin, todes and Khariton studied by the manometer method. At 210-320° decomposition goes with significant speed, which does not depend on the initial pressure of the vapors of methylnitrate, i.e., a reaction of the first order. Filling a container with glass tubes, which increased the surface-to-volume ratio a few times, did not change the speed of the reaction. This indicates the homogeneous flow of the disintegration of methylnitrate in the conditions of given the experiments. The speed of reaction was also not changed with the addition of the products of disintegration to the methylnitrate. This means that autocatalysis is not observed. By the magnitude of the speed constant and its dependency on the temperature kinetic coefficients were calculated (on the assumption that the reaction is monomolecular): energy activation E is (39,500 kal/mol) and pre-exponential factor $B(10^{14.4})$. With respect to the chemical affinity of the disintegration of methylnitrate, the authors assumed by analogy with the disintegration of methylnitrite that the first stage of the process is the detachment of nitrogen peroxide with formations of alkoxyradical.

A more complete idea about the mechanism of decompositon of alkyl mononitrates was obtained by Leva during a study of the disintegration of ethylnitrate. Application of new methods of research — infrared spectroscopy and gas chromatography — made it possible to discover quantitatively determine such intermediate products of disintegration, which earlier escaped the attention of the researchers.

The disintegration of ethylnitrate is a complicated process and constitutes basically a sequence of such reactions:

$$C_2H_5ONO_2 \rightleftarrows C_2H_5O + NO_2; \qquad (a)$$

$$C_2H_5O + NO \leftrightarrows C_2H_5ONO; \qquad (b)$$

$$C_2H_5O + NO \rightarrow CH_3CHO + NOH; \qquad (c)$$

$$C_2H_5O \rightarrow CH_3 + CH_2O; \qquad (d)$$

$$2NOH \rightarrow N_2O + H_2O; \qquad (e)$$

$$CH_3CHO,\ CH_2O + NO_2 \rightarrow NO,\ CO,\ CO_2,\ H_2O \text{ and other products.} \qquad (f)$$

The following data is the foundation of separate stages of the shown sequence of reactions.

With the addition of nitrogen peroxide the disintegration rate decreases. Delay of the disintegration with a small content of nitrogen peroxide* is greater the more it is added. This fact indicates that reaction (a) is reversible. The reality of the reverse reaction ($C_2H_5O + NO_2 \rightarrow C_2H_5ONO_2$) is confirmed also by experiments on the decomposition of ethylnitrite in the presence of NO_2, at which the formation of significant quantities ethylinitrate was observed. This shows that the ethoxy-radical which forms during disintegration of ethylnitrite,

$$C_2H_5ONO \rightarrow C_2H_5O + NO, \qquad (g)$$

in the presence NO_2 will form ethylnitrate:

$$C_2H_5O + NO_2 \rightarrow C_2H_5ONO_2. \qquad (h)$$

During the decomposition of ethylnitrate the formation of large quantities of ethylnitrite is observed (up to 70% of the decomposed nitrate), explained by the reaction (b). The nitrogen oxide

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*The addition of large quantities of NO_2 leads to an acceleration of the reaction.

participating in this reaction is obtained at the expense of the reduction of NO_2 formed by aldehydes.

The addition to ethylnitrate of nitrogen oxide leads to the acceleration of disintegration. This should explain the acceleration of the reaction (b) which in turn due to a decrease of the concentration ethoxy radicals delays the reverse stage of the reaction (a). Besides, the yield of ethylnitrite (of course, this is only for moderate times of reaction, during a large duration of it ethylnitrite is also disintegrates), as should be expected, is increased, during moderate degrees of disintegration even to 100%. The same pertains to the yeild of nitrogen peroxide.

Addition of acetaldehyde similar to nitrogen oxide accelerates the disintegration of ethylnitrate. Acetaldehyde rapidly reacts with nitrogen peroxide, decreasing its concentration and due to this braking the reaction of the ethoxy compound with nitrogen peroxide – the reverse reaction of stage (a).

In view of the complexity of the process of disintegration of ethylnitrate, usual calculations (by manometric curves) of the speed constant K, are also not based on its dependency on the temperature – activation energy E and pre-exponential factor B.

It is possible, however, to create such conditions, at which the disintegration rate will indeed be determined by the speed of its primary stage – by the separation of NO_2. This is attained by carrying out decomposition in the presence of nitrogen oxide and acetaldehyde. Nitrogen oxide reacts rapidly with ethoxy radicals and acetaldehyde – with nitrogen peroxide. Thus, the concentration of products of reaction (a) is lowered, a reverse reaction is made and the disintegration rate of ethylnitrate in this case is determined by the flow of reaction (a) from left to right. In these conditions the speed constant of the reaction is determined by the expression

$$K = 10^{\text{[illegible]}} \cdot e^{\frac{-\text{[illegible]}}{\text{[illegible]}}}\ \text{[illegible]}^{-1}.$$

The magnitude of E = 41,230 cal/mol can be considered as the energy of the break of the bond between oxygen and the NO_2 group in ethylnitrate.

For research of the mechanism of disintegration alykl mononitrates are convenient as relatively simple compounds. However as explosives they are not used for various reasons. The greatest practical value are nitrates of polyatomic alcohols — nitroglycerine, nitroglycol and others.

Disintegration of nitroglycerine in vapors, as well as in the liquid state was studied for pressure growth of gaseous products by S. Z. Roginskiy and other researchers.

There is a number of variants of the manometric method. The most simple is with instruments — a test tube with an explosive is connected with a mercury manomertom. Such method can be used (and with limitations) only for nonvolatile explosives, since flying explosives and also volatile products of disintegration would be passed into cold parts of the instrument, especially if one were to start an experiment in a vacuum. Furthermore, in this variant of the manometric method the reaction container inevitably would be filled with vapors of the manometric or sealing liquid.

All these deficiencies are removed in Bourdon type glass manometer (Fig. 2.15). The manometer constitutes a thin-walled glass diaphragm 4 of a crescent-shaped section, which ends in a needle 6. Reaction container 1, in which the batch of the explosive being investigated is placed and connected with the internal space of the diaphragm. The explosive gases forming during decomposition press on the diaphragm, in consequence of which it bends and the needle deviates from the initial position. In tube 5, surrounding the

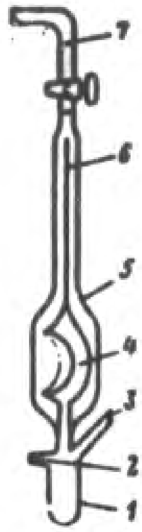

Fig. 2.15. Glass diaphragm manometer. 1 — reaction container, 2 — emptying spout, 3 — spout for introduction of batch, 4 — glass diaphragm, 5 — compensation container, 6 — glass needle, 7 — to thin section.

diaphragm, air is admitted for returning the needle to the zero position. The pressure of the admitted air count on a liquid manometer; the position of the needle is watched with the help of a microscope.

The flow of the disintegration of nitroglycerine to a significant measure depends on the degree of filling of it in a container δ (δ is the relation of the volume of nitroglycerine to the volume of the container) determining, on the one hand, the proportion of nitroglycerine, found in the form of vapors, but on the other — the pressure of gaseous products of disintegration. A strong influence on the flow of transformation can also be rendered by the presence of water. Correspondingly the disintegration of nitroglycerine during small, moderate and large δ is considered, and also in the presence of water.

The disintegration of nitroglycerine with sufficiently small δ, i.e., in vapors flows like the disintegration of methylnitrate with a speed, decreasing in time, according to law, close to the law of a reaction of the first order (Fig. 2.16). As during a monomolecular reaction, the speed of pressure growth does not depend on the concentration of vapors of nitroglycerine. However in a container filled with glass tubes, the speed is greater, which indicates the presence of a heterogeneous reaction to surfaces of the glass,

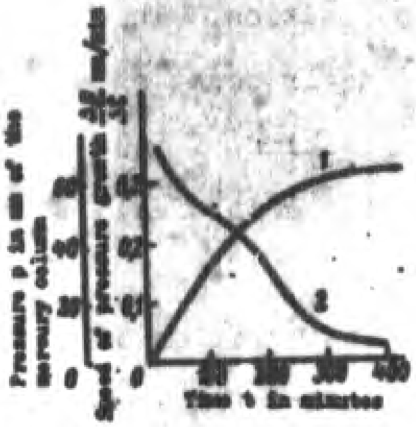

Fig. 2.16. Change in time of pressure of gaseous products and disintegration rate of nitroglycerine in vapors at 140°C. 1) $p = f(t)$, 2) $\Delta p/\Delta t = \varphi(t)$.

flowing along with the homogeneous reaction.

Disintegration nitroglycerine with a moderate δ, when the greater part of it is in a liquid state, flows differently than vapors (Fig. 2.17). First, the disintegration rate in the liquid state is significantly less, secondly, it does not decrease, and in the beginning somewhat increases with time, where the maximum speed is smaller, the larger δ is. If the experiment is conducted in a stream of an inert gas in such a manner so that by it the gaseous products are expelled, then the disintegration rate is not changed from this essentially. This shows that in the given conditions gaseous products of disintegration do not render a noticeable accelerating action on its flow. The third peculiarity of disintegration of nitroglycerine in these conditions is the strong dependency of speed on the temperature, with an increase of temperature by 10° the speed increases approximately 4 times.

Research of the disintegration of nitrates of a number of polyatomic alcohols in the liquid state [trimethylene glycol dinitrate $CH_2ONO_2CH_2CH_2ONO_2$, propylene glycol dinitrate $CH_3CHONO_2CH_2ONO_2$, nitromethane trimethylol trinitrate $NO_2C(CH_2ONO_2)_3$, nitromannite $CH_2ONO_2(CHONO_2)_4CH_2ONO_2$, pentaerythritol tetranitrate $C(CH_2ONO_2)_4$] showed that at initial stages the decomposition flows without essential acceleration. Besides the greater the chain of carbonic atoms of completely esterfied polyatomic alcohol, the faster it is decomposed. Thus, the disintegration rate of nitroglycerine is

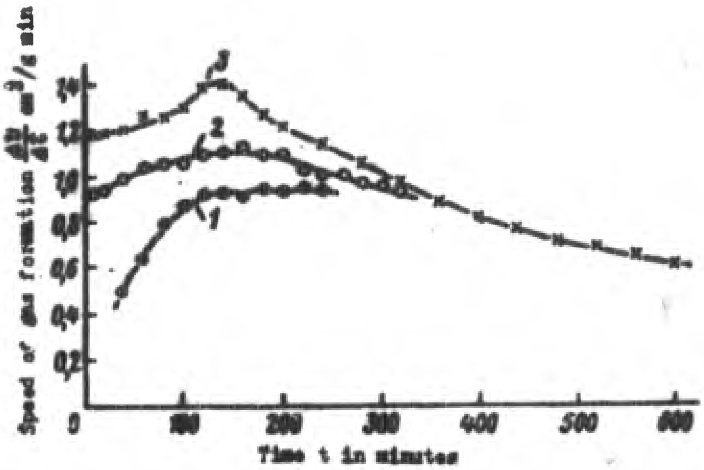

Fig. 2.17. Change in time of the speed of gas formation, expressed in normal cm^3 per minute on 1 g of the substance during disintegration of liquid nitroglycerine at 140°C and moderate δ, correspondingly equal: 1 — $30 \cdot 10^{-4}$; 2 — $12 \cdot 10^{-4}$; 3 — $3 \cdot 10^{-4}$.

greater than nitroglycol, but nitromannite is greater than nitroglycerine. For nitrocellulose the disintegration rate increases with an increase of the content of nitrogen.

As in the case of nitroglycerine, during decomposition of certain nitroesters a strong dependency of the disintegration rate on the temperature is observed. During calculation of kinetic constants this leads to large values of the activation energy E, and also pre-exponential factor B in an expression for the constant of the monomolecular reaction. Thus, for nitromannite $V = 10^{20.6}$, for the tetranitrate $V = 10^{19.8}$, whereas for usual monomolecular reactions in accordance with the theory V does not exceed 10^{14} sec^{-1}.

If the decomposition of tetranitrate not conducted in a fuse state, but in a state of a diluted solution in an inert solvent, then the temperature coefficient of the speed of the reaction turns out to be significantly less. Disintegration rates with moderate temperatures practically are identical for the fusion and solution, but at high temperatures the fusion is decomposed significantly faster. It is possible that here self-heating or an increase with an increase

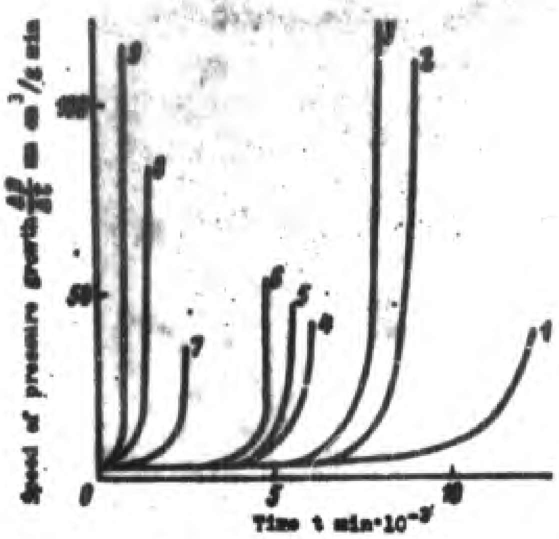

Fig. 2.18. Change in time of the disintegration rate of liquid nitroglycerine at 100°C and large δ, correspondingly equal: 1) $44\cdot10^{-4}$; 2) $59\cdot10^{-4}$; 3) $77\cdot$ $\cdot10^{-4}$; 4) $83\cdot10^{-4}$; 5) $102\cdot10^{-4}$; 6) $106\cdot10^{-4}$; 7) $212\cdot10^{-4}$; 8) $280\cdot10^{-4}$; 9) $700\cdot10^{-4}$.

of temperature of the specific role of the reaction vapors play a role.* In any case, this observation shows that excessively large temperatures of coefficients of speed, which were talked about above, can be caused by side causes.

Disintegration of nitroglycerine with large δ flows essentially otherwise (Fig. 2.18). In the beginning, decomposition goes usually small and weakly increases in time by speed. Then, when the pressure of gaseous products of disintegration and correspondingly their concentration in liquid nitroglycerine attain a certain critical value, decomposition is significantly accelerated. Besides the speed of disintegration rapidly increases in time in conformity with the growth of pressure and can become very great — hundreds and thousands times more than in the beginning of disintegration. The greater δ is, the earlier critical pressure is attained and rapid acceleration of disintegration begins. The higher the temperature, the less solubility of gaseous products in liquid and the greater the critical pressure.

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*The disintegration rate of tetranitrate vapors, as for nitroglycerine, is significantly larger than in the liquid phase.

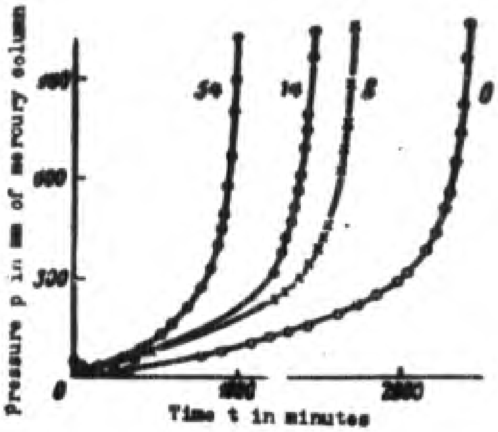

Fig. 2.19. Change in time of pressure during disintegration of liquid nitroglycerine in the presence of small quantities of water at 100°C. Numbers for curves show initial pressure of water vapors in mm of mercury column.

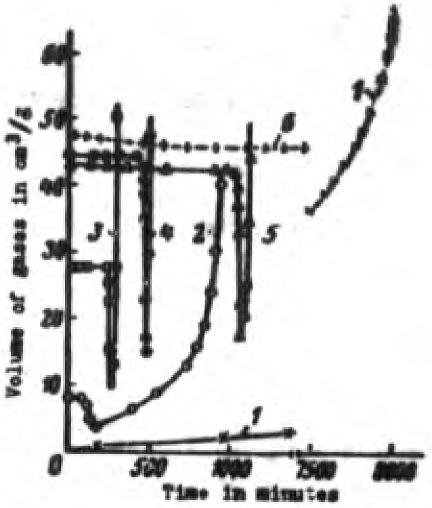

Fig. 2.20. Change in time of volume of gaseous products of disintegration of liquid nitroglycerine at 100°C in the presence of water vapors ($\delta \approx 6 \cdot 10^{-3}$). Pressure of water vapors in mm: 1 – 0; 2 – 116; 3 – 328; 4 – 447; 5 – 467; 6 – 471.

If the container is filled with nitroglycerine almost completely and gaseous products of disintegration do not have possibility to depart from the liquid, then a sharp acceleration of disintegration at 100°C occur at approximately 10 hours, at 80°C in 70 hours, and at 60°C after 620 hour.

The disintegration of nitroglycerine in presence of water has a unique character (Figs. 2.19 and 2.20). When the content of water in nitroglycerines is small (see Fig. 2.19), disintegration in beginning goes faster and the stage of sharp acceleration set in earlier. If there is more water, then the pressure remains constant for a certain time, then due to the transition of water vapors in the liquid phase it sharply drops, after which it starts more or less rapidly to increase (see Fig. 2.20, curves 2-5).

It is necessary to consider that in the presence of water hydrolisis of nitroglycerine occurs; judging from the character of the curve of the change of pressure, it flows by complicated means and is self-accelerated, obviously, as a result of catalytic action of the forming during hydrolisis volatile acids and subsequent the development of oxidizing reactions. If these acids are neutralized (for instance, the connecting with nitroglycerine and a container with soda), then acceleration of disintegration is not observed. Large quantities of water also delay the approach of acceleration (see Fig. 2.20, curve 6).

The total time from the beginning of the experiment to the approach of sharp acceleration in presence of moderate quantities of water is much less than in its absence. Apparently, in case the disintegration of dry nitroglycerine hydrolisis also plays somewhat of a role, but water (as the same catalyst of hydrolisis – acid) will be formed in the very movement of decomposition; the later the approach of acceleration should be explained by the fact that initially nitrogen peroxide is separated, and water will be formed as a result of secondary oxidizing processes relatively slowly.

The described character of the disintegration of nitroglycerine, consisting of two stages – a slow reaction in the beginning and very strongly accelerated hydrolytic and oxidizing reactions, advancing after the accumulation of products of disintegration, – is typical also for many other nitroesters of polyatomic alcohols, for instance nitroglycol, dinitroglycerine, tetranitrate, and in known conditions nitrocellulose as well.

Thermal disintegration of nitrocellulose differs by certain peculiarities. Nitrocellulose as a high-molecular substance is at usual temperatures of decomposition in the solid state, along with this it possesses a physically complicated structure, usually a well-developed surface, and does not constitute, as a rule, a chemically uniform compound. Finally, in obtaining nitrocellulose different, frequent unstable, difficult to remove completely impurities are formed which can accelerate its disintegration. All these circumstances essentially complicate the flow of disintegration.

Decomposition of nitrocellulose at increased temperatures always flows with acceleration. The character and magnitude of this acceleration to a strong degree depends on conditions. The acceleration, although relatively small, is observed even in the case when disintegration is conducted in a vacuum with continuous evacuation of forming gases. This can be seen from the curve, depicting the speed of the decrease and weight of nitrocellulose during thermal disintegration in a vacuum obtained with the help of Mac-Ben scales (curve 4 in Fig. 2.21): in beginning of the experiment the speed of the decrease and in weight grows. If one were to determine separately the speed of the formation of gases, which are condensed in a trap with liquid nitrogen and the gases, which pass

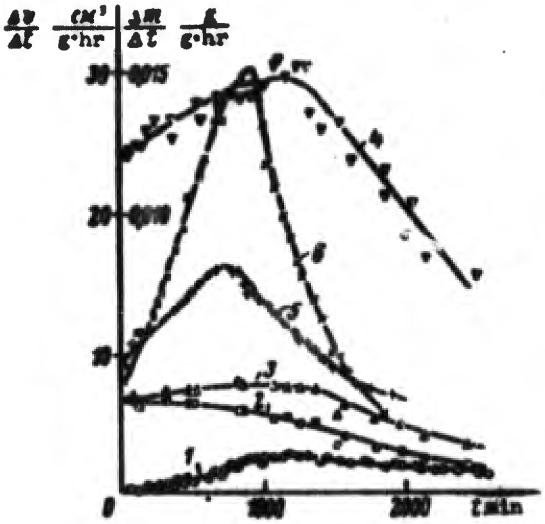

Fig. 2.21. Changes in time of speed of decomposition of nitrocellulose at 145°C. a) in a vacuum during pumping out of gases, 1 — noncondensing gases, 2 — condensed gases, 3 — total quantity of gases, 4 — loss in weight. b) at quasiconstant pressure (10 mm) — 5, c) without evacuation gaseous products of disintegration (pressure during achievement of maximum speed ~500 mm) — 6. Along the axis of ordinates deposited for curves 1, 2, 3, 5 and 6 speed of gas forming in cm³/hr, and for curve — 4 speed of loss in weight g/hour on one gram of the parent substance.

through it not being condensed, than it turns out that first they drop in time, and the speed of formation of non-condensed gases is strongly increased. This is talking about the fact that acceleration during thermal disintegration of nitrocellulose in a vacuum has a complicated character: at least two reactions occur, where the speed of the secondary reaction strongly increases in time, the speed of the primary reaction is increased less, or even — at high temperatures — not showing an increase, but will drop from the very beginning of the experiment.

The influence on the decomposition of nitrocellulose of its gaseous products can be eliminated not only by means of carrying out disintegration in a vacuum, but also by carrying out the experiment in a current of inert gas, as this is done during determination of the stability of nitrocellulose by a Vill' probe (see page 172 below). The quantity of separated nitrogen grows in these conditions proportinately to the time (Fig. 2.22). This means that the absolute velocity of the separation of nitrogen is constant, and increases relatively.

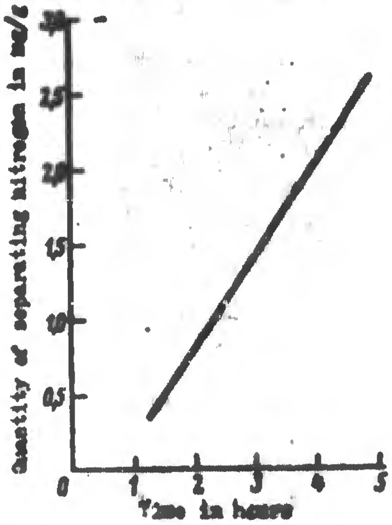

Fig. 2.22. Dependence on time and quantity of decomposed substance (separated nitrogen) during decomposition of nitrocellulose in current of inert gas according to Vill'.

If one were to conduct decomposition in an empty container, and did not free forming gases, then the speed of gas forming grows stronger than at constant freeing of gases. This acceleration usually will add a catalytic action of gaseous products of disintegration. Such an explanation contradicts, however, the relatively small magnitude of acceleration and its weak dependency on pressure (see Fig. 2.21, curve 6). Furthermore, acceleration is observed also during continuous freeing of gases, and at a certain constant (average) pressure of gaseous products of disintegration, which was maintained by their periodic freeing (see Fig. 2.21, curve 5). Therefore one should consider that the influence of gaseous products of disintegration in these conditions is basically not catalytic and is determined by the reaction of their reacting in components with each other, with condensed products of disintegration and, possibly with an unreacting substance.

The decomposition of nitrocellulose in distinction from nitroglycerine is weakly accelerated by water vapors (Fig. 2.23). If, however, simultaneously with water oxygen or an acid are present, then in a certain time after the start of the experiment a sharp acceleration of gas forming occurs. The action of oxygen consists in the oxidation of nitrogen oxide to NO_2; the latter with water will form acids, provoking hydrolytic disintegration of nitrocellulose.

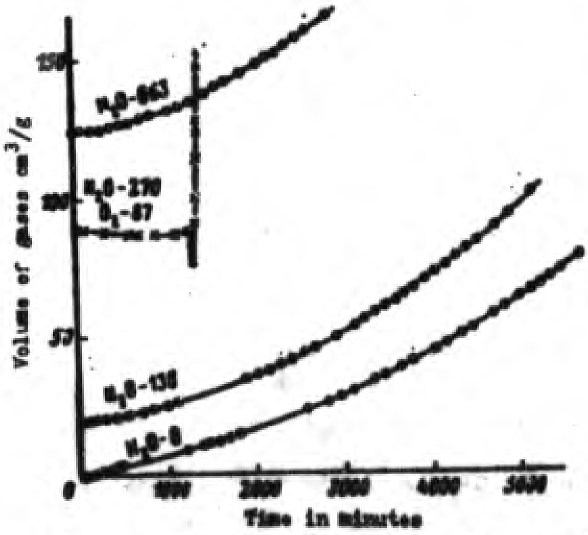

Fig. 2.23. Change of volume of gaseous products during disintegration of nitrocellulose (at 120°C) in the presence of water and oxygen. Numbers with curves give the pressure of water vapors and oxygen in mm of mercury column at the temperature of the experiment.

The distinction of the disintegration of nitrocellulose in the presence of water vapors from the disintegration of nitroglycerine can be combined with various speeds of reduction of the primary forming nitrogen peroxide. During disintegration of nitroglycerine this speed is small, during disintegration of nitrocellulose it is great, and it is necessary to oxygen, in order to transfer the nitrogen oxide to the dioxide.

If in the reaction container nitrogen peroxide a nitric acid is directly introduced, then the disintegration of nitrocellulose is accelerated. The greatest accelerating action is rendered by an acid of average concentration; weak and concentrated acids give less acceleration.

From all of the considered data it follows to conclude that the disintegration of nitrocellulose is a complicated reaction, including even during freeing of gaseous products of the disintegration by at least two steps. In the presence of gaseous products of disintegration the reactions flow even more complicated. Moreover, there is a basis to consider that during disintegration of nitrocellulose topochemical effects appear. It was determined that the disintegration rate depends on the magnitude of the particles of nitrocellulose. The less particles, i.e., the more specific surface of the substance the greater the disintegration rate. This fact shows that the reaction to surfaces of particles goes faster than to a volume which is characteristic for topochemical reactions. Further it is established that during decomposition of nitrocellulose under a layer of an inert liquid, for instance xylene, paraffin, in water at 130-135°C under pressure, in the presence of liquid nitro compounds of aromatic hydrocarbons, the disintegration rate is less than in the absence of a liquid. Such influence of covering the surface of a solid with a liquid layer also indicates the topochemical character of the process (see p.144).

During removal of gaseous products of disintegration the speed of it strongly depends on the temperature, with an increase of temperature by 10° it increases 3.6-4 times. By a speed of decomposition, flowing without the removal of gaseous products, the temperature has less influence.

3. Slow Chemical Transformation of Nitro Compounds and Nitramines

Thermal disintegration of nitro compounds and nitramines (trinitratoluene, trinitrophenylmetylnitramine, cyclotrimethylenetrinitramine, ethylenenitramine and others, as in the case of nitro esters, starts with a small speed, which at first increases, and then drops due to a decrease of the quantity of the unreacting substance (Fig. 2.24). The constant of the initial disintegration rate in the case of a polynitro compound of an aromatic group and hexogene is much less than for nitroesters. Other nitramines are close in this respect to nitroesters (see Table 2.5).

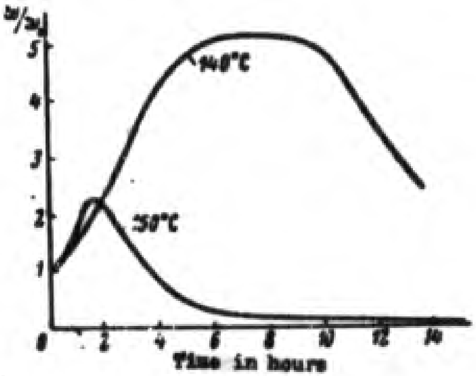

Fig. 2.24. Change of speed of gas forming during disintegration of liquid tetryl at 140 and 150°C.

Nitro compounds and nitramine differ from nitroesters according to the character of the flow of decomposition, and also the magnitude of autoacceleration of the reaction. In the first case, acceleration usually starts from the beginning of the disintegration, is developed gradually and not as great, as during disintegration of nitroesters.

For a number of substances (tetryl, trotyl, hexogene) the autocatalytic nature of acceleration is determined; the addition of

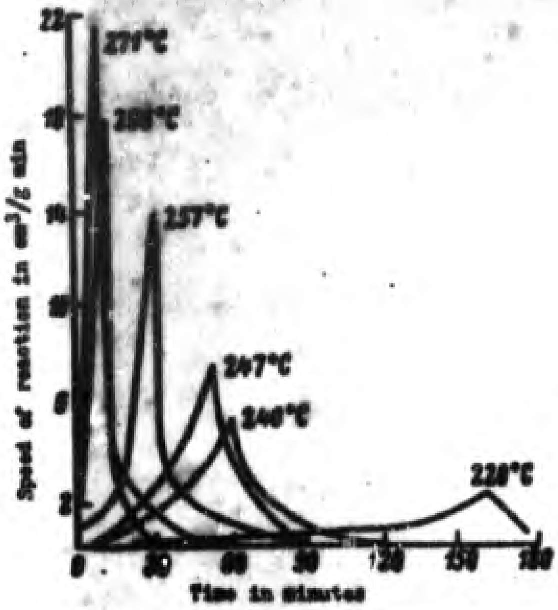

Fig. 2.25. The influence of temperature on movement of decomposition of trotyl.

products of the reaction to pure explosive leads to a significant increase of the speed of decomposition. Gaseous and condensed substances do not appear as catalysts. Due to this change 5, if self-heating is excluded, does not render such a strong influence on the flow of disintegration as was observed for certain nitroesters.

For trotyl it is established that the higher the temperature of the experiment, the greater the maximum of speed and the faster it is attained (Fig. 2.25). The influence of different additions to the disintegration of trotyl was investigated, not one of them rendered retarding action, conversely, many additions accelerated the disintegration, but at high temperatures, when decomposition ended with detonation, period of delay to the detonation was reduced. The strongest accelerating action was rendered by hopcalite,* a complex compound α-nitroso-β-naphthol with iron, manganese peroxide and diphenylamin. Usually detonation of trotyl occurs at heating then, when a definite content of autocatalyzing products are accumulated, which requires a certain time. However, four additions (hopcalite, ammonium bichromate ammonium, iron oxide and barium hydroxide) brought on detonation at

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*A mixture of oxides of manganese, copper, cobalt and silver, used as a catalyst of the reaction of oxidation carbon oxide at a low temperature.

300°C immediately without noticeable preceding decomposition. The cause of this should be looked for in the energetic exothermic reaction between trotyl and the addition.

In vapors trotyl in contrast to nitroglycerine is decomposed significantly slower than in the liquid state.

Decomposition of liquid or dissolved <u>hexogene</u> at 200-300°C flows according to the law of the reaction of the first order with the developed by means of accumulation products of disintegration by autocatalytic acceleration. At low temperatures autocatalysis is expressed stronger than at high. As in the case of tetranitrate, in a diluted solution the disintegration rate of hexogene is less than at the fused, this difference is small at relatively low temperatures (200°C), but increases with the temperature. In other words, the temperature coefficient of speed for fusion is greater than for a solution. This leads to significantly greater activation energy for a fusion and also to an increased value of the B factor.

Table 2.4. Dependency of the Disintegration Rate of Tetryl on its Concentration

Time in hours	Number of moles of gas per mole of tetryl		
	Pure tetryl	33% solution in trotyl	16.6% solution in trotyl
1	0,18	0,23	0,19
2	0,49	0,63	0,54
3	0,86	1,00	0,84
4	1,19	1,28	1,06
5	1,46	1,50	1,20
6	1,64	1,65	1,43

The decomposition of <u>tetryl</u> was studied by Khinshel'vud. As determined by experiments on the decomposition of tetryl at 150°C in fusion and in trotyl* solutions, the speed of its disintegration does not depend on the concentration (Table 2.4). Along with the monomolecular an autocatalytic reaction flow, according to Khinshel'vud the forming during disintegration picric acid is autocatalysis. The change of speed in time well corresponds with the expression (2.28) for autocatalytic reaction. At 140°C the constant of speed of autocatalytic reaction is 5.35 times more than the constant of monomolecular. Experiments on the decomposition of tetryl with earlier added picric acid immediately showed a high speed, which corresponded to that expected by the calculation.

The catalytic action of picric acid on the disintegration of tetryl was confirmed by Roginskiy and Lukin who determined the delay time of the detonation tetryl in closed tubes. Pure tetryl detonated (at 156°C) in 29 minutes, with the addition 5 and 20% picric acid – in 21 minutes and 13.5 minutes.

The disintegration of tetryl was studied at temperatures above, as well as lower than the fusing temperature. Besides it was revealed that the disintegration rate of liquid tetryl is 50-100 times more than the solid. Furthermore, the speed of disintegration of solid tetryl is much greater than liquid. In the process of decomposition condensed products are formed, being dissolved in tetryl, they lower its fusing temperature and part of the solid matter passes into a liquid state. Since the liquid is decomposed faster, the speed of disintegration occurs in this case by two causes: due to the gradual transition of solid tetryl to a liquid and due to the accumulation of autocatalysis.

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*Trotyl with this temperature is decomposed extraordinarily slowly as compared to tetryl, and it can be considered as an inert solvent.

4. Expolsives Which Decompose in Solid State

In the preceding divisions we considered the laws of disintegration of those expolsives which (with the exception of nitrocellulose) at temperatures of the experiment are in a liquid state. For many explosives (chiefly the salt of heavy metals) the temperature of fusing is higher than the temperature of detonation, for others – the temperature of fusing is sufficiently high, and they are decomposed with significant lower speeds than this temperature, in the solid state.

As established above, self-accelerated disintegration of solids can be attributed to two cases, topochemical and chain. Topochemical disintegration in turn flows in different ways with respect to the dependency of speed of the reaction and quantity of the reacting substance on time. One type of disintegration is observed with a small and constant number of nuclei, others – with large numbers of nuclei.

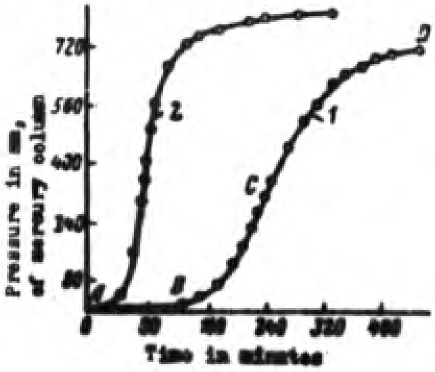

Fig. 2.26. Thermal disintegration of calcium azide. 1 – under a layer of paraffin, 2 – without paraffin.

<u>Topochemical disintegration</u>. An example of topochemical disintegration of first type is the decomposition of <u>calcium axide</u> CaN_6 during heating.

As manometric research has shown, at temperatures of 100-140° curves, depicting the change in time of the pressure of nitrogen forming during disintegration, have an S-shaped form (Fig. 2.26). The process of decomposition of calcium azide can be divided into three stages,

1) induction period with very small and practically constant speed (section AB on curve),

2) a sharp increase of the disintegration rate (section BC) and

3) a drop of speed (section CD).

The induction period in the case of calcium azide is caused to a significant measure by the action of impurities, destroying nuclei of the reaction and thus preventing its development. Exhausting these impurities makes possible the growth of nuclei and the speed of reaction starts to grow rapidly.

In the period of the acceleration of speed the reaction well follows the topochemical law for the case of constant number of nuclei. Practically this case is realized by means of preliminary heating of the azide at a higher temperature so that the nuclei are formed. Then the temperature is lowered and decomposition conducted at this temperature, when the new nuclei practically were not formed, and only the growth of nuclei of the reaction occured,* appearing during preliminary heating. It is possible to establish quite graphically the fulfillment of the equation (2.46), constructing the graph lg w-lg x. With this a straight angle of inclination with the tangent equal to 2/3 should be obtained. Figure 2.27 gives the straight line obtained during

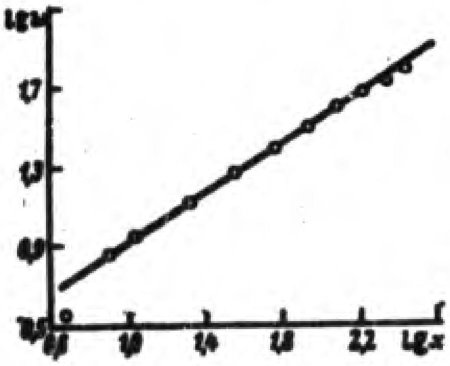

Fig. 2.27. Dependency of disintegration rate of calcium azide on the quantity of the decomposed substance.

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*Formation of nuclei of a black color well visible on the background of white crystal aggregates, could be to observed visually even with a small increase.

experiments, where tg α = 0.65. The latter period — the drop of speed — mathematically obeys the monomolecular law.

Calculation of the energy activation showed that in the interval of temperatures of 80-100°C E = 20,000 cal/mol. It is interesting that with an increase of temperature energy activation does not remain constant, but increases, attaining 34,000 cal/mol at 140°C.

The introduction into the test tube with calcium axide of paraffin in such a way, so that the crystals were under a layer of liquid, leads to sharp braking of the disintegration (see curve 1, Fig. 2.26). The braking action of paraffin is observed also when it is introduced during an already flowing reaction: the speed immediately becomes 40 times less. An analgous influence of paraffin was later established also during decomposition of silver oxalate and during thermal disintegration of nickel formate.

The mechanism of the action of paraffin is not completely clear. The most probable cause of braking the reaction is deactivation by the paraffin of any of the intermediate products of the reaction, which accelerate the process. This influence has, apparently, a general character and may be used as one of the criteria for establishing the topochemical mechanism of the reaction.

Garner and Reeves studied the influence of ultraviolet irradiation on the subsequent thermal decomposition of calcium azide. Irradiation strongly reduces the induction period and increases the disintegration rate. The exponential law of growth of speed is maintained.

Similarly with calcium azide by type of disintegration many other explosive and nonexplosive substances are decomposed: silver oxalate, mercury oxide, silver oxide, barium azide and strontium azide.

<u>Trinitrotridzidobenzoyl</u> apparently is decomposed by the second type of topochemical disintegration (when the number of nuclei are large and products of the reaction rapidly cover the surface of the crystal). At low temperatures (100°C and lower) disintegration flows according to the equation

$$C_6(NO_2)_3(N_3)_3 = C_6(NO)_6 + 3N_2$$

with formation of hexonitrozobenzoyl and nitrogen. The dependency of the quantity of reacting substance on the time is shown in Fig. 2.28. Analysis of curve showed that decomposition very closely follows the equation (2.50). Deflections of the constant, calculated for that equation by experimental data do not exceed 1.5% from the mean value.

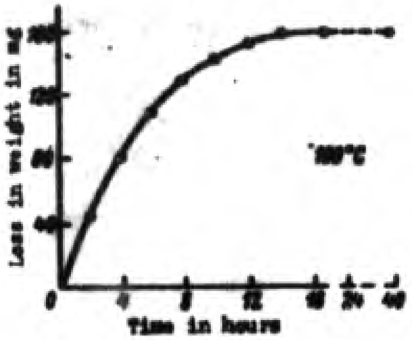

Fig. 2.28. Thermal disintegration of trinitrotriazidebenzene.

Comparison of values of the constant of speed at various temperatures (20-100°C) gives an activation energy of disintegration of solid trinitrotriazidobenzene equal to 32,300 cal/mol.

<u>Chain disintegration</u>. Characteristic for topochemical process is the presence of a section of acceleration, on which the speed increases in time by the exponential law caused by the growth of three-dimensional nuclei of the reaction.

For certain solids (explosive and nonexplosive) a significant period of acceleration is also observed, but the speed grows in time not by exponential, but by the coefficient law ($\frac{dx}{dt} = Ae^{\varphi t}$), characteristic for chain reactions. As an example, it is possible to conduct decomposition of <u>lead trinitroresorcinol</u> $C_6H(NO_2)_3O_2Pb \cdot H_2O$ (Fig. 2.29). During heating of this substance in vacuum to 120°C,

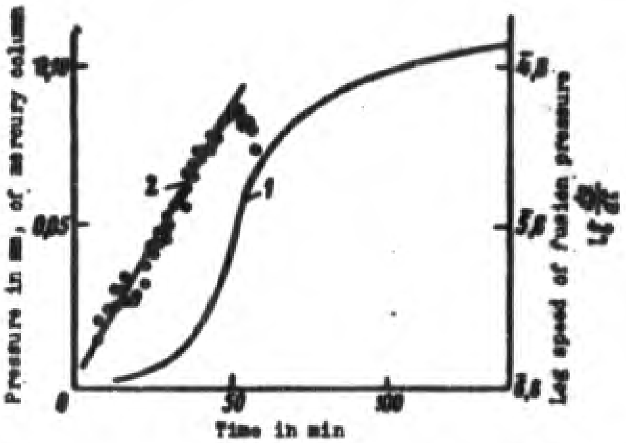

Fig. 2.29. Thermal disintegration of lead trinitroresorcinol according to Kheyls. 1) $p = f(t)$; 2) $\lg \frac{dp}{dt} = \varphi(t)$.

first of all the water of crystallization is lost, where dehydration does not evoke a change of the form and transparency of the crystal. After dehydration thermal decomposition follows, and, if the temperature is higher than 225°, it is ended by a detonation. An analogous character of curves for the section of acceleration was observed during decomposition of oxalates of certain heavy metals and permanganates.

The results of the research of the disintegration of solid explosives, accelerated by the coefficient law, as Semenov showed, well agrees with the chain system of the development of the reaction. This system makes it possible to explain quantitatively the presence and duration of the induction period, the influence of breaking up, the dependency of the delay of detonation on the temperature, etc.

Only the induction period will be explained, the mechanism of which in this case is different than during topochemical disintegration of calcium azide. In the latter case, the induction period is caused by the presence of impurities, braking the autocatalytic reaction. At chain disintegration Semenov considers the induction period is apparent, which is obtained as a result of slowness of development of the chain. At first, when the pressure is very little and its change cannot be measured by the instrument used, the impression of absence of reaction is created. Actually the reaction flows, being accelerated by the same law from the very beginning and to the end of the period of acceleration, but we start to notice it only when the pressure of the gases formed attains a certain value. Confirmation of this point of view is the fact that the product of the magnitude of the induction period on φ always preserves a constant velue, in accordance with the expression (2.41) this requires a chain theory.

5. General Regularities of Slow Chemical Transformation of Explosives

Chemical transformation of explosives at heightened temperatures starts, as was indicated, from a primary reaction, which is monomolecular or at least flows according to the law of a reaction of the first order. Characteristics of this reaction can be established, studying the initial stages of the process, when the concentration of products of the transformation is small and they still do not render an essential influence on its movement.

If the products of decompositions are gaseous, it is possible to decrease their influence, can conducting disintegraion with small undrenching degrees of filling the container, in a current of inert gas or in a vacuum, with freeing of the forming gases. With this the pressure of the products of disintegration on the liquid is small, if their solubility in condensed the explosive is small then the concentration of products in it will be low.

The influence of reactive products of a primary reaction to the flow of transformation of an explosive can also be prevented: adding to it such substances (stabilizers), which quickly react with the products of the reaction, form a compound which does not render influences on disintegration.

Studying the temperature dependency of the speed of a monomolecular reaction, it is possible to establish its kinetic constants, activation energy and pre-exponential factor B.

For the first time such an analysis of the kinetics of the disintegration of explosives was conducted by Roginskiy on the basis of his own experimental data and materials of preceding works. This analysis revealed certain kinetic peculiarities of the primary disintegration of explosives.

Explosives disintegrate with a noticeable, measurable speed at moderately high temperatures (100-200°C), i.e., the speed constant of their disintegration is sufficiently large. At the same time this disintegration is characterized by a large temperature coefficient of speed, with an increase of temperature by 10° the speed of the disintegration rate for many studied explosives is increased 4 times. Such a great temperature coefficient of speed inevitably signifies a high energy of activation.

Actually, at a temperature T_2 the constant of speed of the reaction

$$K_2 = Be^{-E/RT_2},$$

and at T_1 the same constant

$$K_1 = Be^{-E/RT_1}.$$

Hence the temperature coefficient of speed is

$$\frac{K_2}{K_1} = \frac{e^{-E/RT_2}}{e^{-E/RT_1}}. \qquad (2.54)$$

By log is obtained

$$\ln\frac{K_2}{K_1} = -\frac{E}{RT_2} + \frac{E}{RT_1}$$

or

$$\ln\frac{K_2}{K_1} = \frac{E}{R}\,\frac{T_2 - T_1}{T_1 T_2},$$

whence

$$E = R\frac{T_1T_2}{T_2 - T_1}\ln\frac{K_2}{K_1}. \qquad (2.55)$$

Thus, if at the given value of the product T_2T_1 the relation of K_2/K_1 is great, then the value E should be great. On the other hand, inasmuch as already at a moderate high temperature the constant K is significant, then with a great activation energy E the pre-exponential factor B, equal to the product of $Ke^{E/RT}$, should be also large.

Actually, as one can see from Table 2.5, for many explosives the energy E is great, being within the limits of 40,000-60,000 cal/mol, the same pertains also to the magnitude of B, lying between 10^{18} and 10^{28}.

The fact that the activation energy of an explosive is great, by itself would not be surprising. The ability to explode it does not certainly suggest as we saw (p. 36), the instability of the molecule. This ability is determined by the relationship of the energy of the reaction of disintegration of the molecule, which exists the transformation of neighboring molecules, and the activation energy, measuring the stability of the molecule with respect to energy influences.

Otherwise it is a matter with the large values of the V factor. According to the theory V cannot be essentially larger than the frequency of intramolecular oscillations, i.e., it should be within the limits of 10^{12}-10^{14}. Therefore, the establishment by Roginskiy of much larger values of V evokes significant interest. It is possible to allow that this regularity is a fundamental characteristic of explosives.

The suggestion about the presence of long chains, consisting of

Table 2.5. Kinetic Characteristics of Primary Reaction of Disintegration of Different Explosives

Explosive	Interval of temperature in °C	Activation energy E cal/mol	lg, V	Half-life* at a temperature of 120° C per hour	Note
Methylnitrate	212—239	39 500	14,4	7120	
Ethylnitrate	161—181	41 230	16,25	921	
Nitroglycol (in vapors)	140—170	35 700	14,3	69	According to various operations
Nitroglycol	96—105	39 000	15,9	119	
Nitroglycerine (in vapors)	150—160	36 000	15,5	6,4	
Nitroglycerine	125 - 150	45 000	19,2	129	
Nitroglycerine	90—125	43 700	18,64	89	According to various operations
Nitroglycerine	75—105	40 300	17,1	40	
Propylene gylcol dinitrate	80—100	37 400	15,2	77	
Trimethyleneglycol nitrate	85—110	38 100	15,2	188	
Nitromethane trimethyl-trinitrate	75—95	36 400	15,3	17	
PETN	145—171	39 000	15,6	240	According to various operations
PETN	160—225	47 000	19,8	420	
PETN in solution	171—238	39 500	16,1	142	
Ethylenediamindinitramine	230—357	40 000	13,1	2,7·10⁵	
Ammonium nitrate	243—361	40 500	13,8	10⁵	
Pyroxylin No. 1 (13.35% N)	135—160	43 400	17,5	856	
Ethylenedinitramine	184—254	30 500	12,8	2,8	
Tretyl	220—270	53 500	19,0	5,8·10⁴	
Picric acid	—	57 500	23,0	1,8·10⁶	
Hexogene	213—299	47 500	18,5	1,6·10⁴	
Hexogene in solution	—	41 000	15,46	4,2·10³	
Octogene	—	52 700	19,7	7,8·10⁵	
Liquid tetryl	129,9—136,6	60 000	27,5	142	According to various operations
Liquid tetryl	—	55 500	24,5	467	
Liquid tetryl	211—260	38 400	15,4	174	
Solid tetryl	—	52 000	22,5	305	
Solid tetryl	—	36 600	12,7	8700	
Calcium azide	80—100	20 000	—	—	
Trinitrotriazidobenzene	20—100	32 300	—	—	
α-Lead azide	245—275	55 000	—	—	
β-Lead azide	237—282	40 000	—	—	
Lead trinitroresorcitor	225—255	46 700	—	—	
Potassium picrate	270—290	42 000	—	—	
Mercury fulminate	100—115	30 000	—	—	

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*Half-life at 120°C is calculated by the values of E and B, obtained in the interval of temperatures, shown in the second column of the table, for that aggregate state, in which the explosive is located in this interval of temperatures.

10^6-10^7 links would explain the large values of V. However the experiments set in connection with this on the decomposition of nitroglycerine in solutions did not confirm the given assumption. Further research showed that large values of B are not an inevitable peculiarity of explosives.

For a number of explosives, also including certain nitroesters of alcohols moderate values of E and normal values of B were determined. Further, for one of the nitroesters (tetranitrate) and one nitramine (hexogene), which give during decomposition in pure form large values of B, during decomposition in a solution the pre-exponential factor V has a normal magnitude. All of this indicates the fact that large values of the B factor are not a characteristic of monomolecular reaction, but are caused by certain peculiarities of the flow of the reaction of disintegration of individual explosives.

One of such peculiarities may be the increase of volume of gaseous products, formed by a single mass of explosives, with an increase of the temperature of disintegration. If, besides, the relation of speeds at two temperatures are characterized by the relation of absolute volumes of gases, separated in a unit of time by a unit of weight of the explosive, without calculation of the shown change of volume, then an oversized value of the temperature of the coefficient of speed will be obtained. During calculation by the formula (2.55) this will lead to oversized values of the magnitude of E, and consequently, B as well.

Another cause of obtaining large values of V may be the fact that the reaction of disintegration consists of two steps: endothermic and reversible transition of the parent substance A in the intermediate product C and the irreversible reaction of disintegration of the latter in the final products D:

$$A \rightleftarrows C \rightarrow D.$$

Then with an increase of temperature the total speed of the reaction increases by two causes: due to an increase of the concentration of the intermediate product C and due to an increase of the speed of transition of it to the final product D. As a result, the conducting calculation for a single-stage primary reaction, will obtain an oversized value of the temperature coefficient, and consequently also a larger value of E and the B factor.

Other mechanisms are also possible, which lead to oversized temperature coefficients. Thus, if during decomposition there are short and therefore difficultly revealed chains, the length of which increase with the temperature, if the place is self-heating, growing with the increase of temperature, if with an increase of temperature the proportion of a more rapid reaction in the gas phase increases, then all of these factors can lead to heightened values of the magnitudes of E and B.

A more precise definition of these questions for specific explosives should be the subject of further experimental research.

In any case, many typical explosives do not show with respect to characteristics of monomolecular reaction any essential distinctions from nonexplosive substances.

More characteristic for explosives is their self-accelerated transformation, developed by measure of the accumulation of products of disintegration. This transformation flows with speeds, much greater, than the primary reaction is completely exothermic and can lead to thermal appearance of a detonation. Autoacceleration of a reaction depends not only on the properties of the substance, but on the conditions, in which its disintegration flows as well. We saw that nitroglycerin in vapors or at small degrees of filling the container is decomposed without essential acceleration and only during large degrees of filling the container and especially in the presence of small quantities of water is sharp acceleration of process is observed. In case of nitrocellulose for the approach of sharp acceleration not only water is required, but also oxygen.

The mechanism of autoacceleration may be, as already noted, different autocatalytic (for instance, trotyl, tetryl, hexogene) hydrolytically-autocatalytic (for instance, nitroglycerine) chain (for instance, lead trinitroresovcinol), topochemical (for instance, calcium azide), acceleration may also be caused by the flow of consecutive reactions, or progressive fusion.

Important characteristics of self-accelerated disintegration of explosives are the magnitude of maximum speed and time of its achievement.

A practical value of slow chemical transformation consists in that it determines chemical stability of explosives. During storage of explosives which may be very prolonged, or during technological processes of its processing, if they are produced at heightened temperatures (drying, rolling of powders, molded charges and others), to a certain degree decomposition of the explosive can cccur. If the process of decomposition is limited by the stage of the primary reaction, then the degree of decomposition usually is small, since for explosives applied in technology the constant of the speed of these reactions is small. It is another matter, if self-accelerated process is to be developed successfully. When the maximum speed of a reaction is great and is attained fast, then decomposition of explosives can occur to a significant degree, essentially worsening its subsequent action. In conditions of hampered heat withdrawal during strong autoacceleration, decomposition may end in detonation.

With respect to the characteristics of autoacceleration of the disintegration of explosives, a different chemical structure strongly differs from each other. Thus, a nitro compound and nitramine are decomposed with relatively small acceleration. Inasmuch as simultaneously with this the constants of speeds of the primary reaction of the disintegration of these explosives are also small, then their stability is sufficiently great and determination of it is not anticipated in a number of standard tests. Conversely, for nitroesters in certain practically real conditions, when gaseous products of transformation are maintained in the explosive, acceleration of disintegration can become very large and maximum speed can hundreds and thousands of times exceed the initial speed of decomposition. Since along with this the primary reaction during disintegration of nitroesters flows with greater speed than nitro compounds, then the maximum speed by an absolute value can become very great even at low temperatures. This can lead to deep decomposition of the substance, and with large quantities to thermal self-ignition as well. By these causes the problem of chemical stability of nitroesters remains urgent.

Significant acceleration is observed also in the case of certain solid explosives, decomposed by topochemical or chain law. However these explosives are used only in the form of small charges in capsule-detonators and for thermal the appearance of a detonation such conditions are not favorable. Therefore the question on the stability of these explosives is not so sharp as in the case of nitroesters.

For an illustration of these relationships Fig. 2.30 shows the change of the disintegration rate in time for tetryl, notroglycerine and mercury fulminate. Along the axis of the ordinates is put the relation of speed in moment of time t to its initial value.

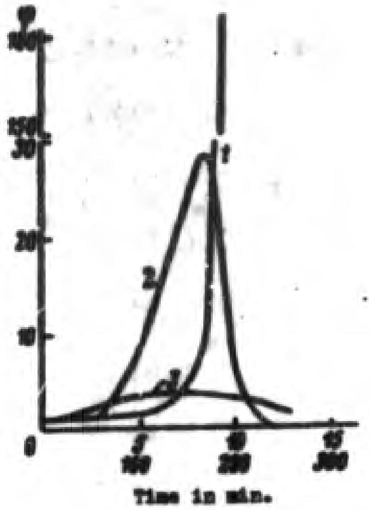

Fig. 2.30. Change in the time of the disintegration rate of nitroglycerine (1) and mercury fulminate (2) at 80°C and tetryl (3) at 140°C. The higher time pertains to tetryl, the lower — to nitroglycerine and mercury fulminate. Speed is expressed by the relation $\varphi = \frac{w_t}{w_{initial}}$, where for mercury fulminate for the initial speed is taken a speed of t = = 50 hour.

In those cases, when acceleration of disintegration is very great, i.e., when very small quantities of products of disintegration or impurities strongly increase the speed of decomposition, it is possible to prevent acceleration. This is attained by the addition to the explosive of small quantities of such substances, which react rapidly with accelerating impurities or products of disintegration. Such substances are called stabilizers, they are widely used in contemporary smokeless powders.

Above in examining the decomposition of tetryl a significant (10 times) increase in speed during transition from a solid to liquid aggregate state was noted. Such influence of the aggregate state has a general character and was observed for all studied in this respect explosive (and nonexplosive) substances (tetryl, tetranitrate, hexogene, trinitrooxyphenolmethylenenitramine and others). It allows the acceleration of decomposition of many solid fused explosives to become larger than during decomposition of the same explosives in liquid state. This is observed, when condensed final or intermediate products of disintegration are formed, which, being dissolved in the parent substance, progressively shift it into liquid state. It follows from this that if on conditions of work important to ensure as large as possible stability of the explosive, then it is not necessary to approach the temperature of its fusing, and all the more so to change it or to add impurities to the explosive which lower this temperature. If in conditions of work with a high temperature cannot be lowered, then it is expedient to use an explosive with a temperature of fusing, lying higher than the temperature of use.

This influence of an aggregate state on the disintegration rate of an explosive should be considered also during selection of the temperature for a comparative test of a different explosive for stability. Imagine two explosives, disintegrating with identical speed both in solid and in liquid state, but having various temperatures of fusing, for instance 130 and 140°C. If one were to conduct a test at a temperature of 135°C, lying between the fusion temperatures of these explosives, so that one substance will remain solid and the other will be liquid, then for the liquid a much higher speed can be obtained and it will be considered less stable. This conclusion will appear erroneous, since with usual temperatures of storage both explosives will be in a solid state and the speed of their disintegration will be identical.

Namely in this also is considered the cause of the erroneous conclusion about the less stability of alloys of tetranitrate with trotyl, done by a series researchers, comparing the disintegration rate of tetranitrate (fusing temperature fusing 140°C) and given alloys (fusing temperature <130°C) at 135°C. Therefore a comparative test on the stability should be conducted at such a temperature at which the explosive being tested is in an identical aggregate state. In particular, if one were to compare the disintegration rate of tetranitrate and its alloy with trotyl at a temperature, lying higher than the fusing temperature, it turns out that trotyl, as one should be led to expect, does not have a negative influence on the disintegration rate of tetranitrate.

CHAPTER III

THE STABILITY OF EXPLOSIVE SUBSTANCES

The stability of an explosive is determined by the speed of change of its physical and chemical, and consequently also explosive properties with the flow of time. The smaller this speed, the greater the stability of the explosive and vice versa.

There are two kinds of stability: physical and chemical.

Physical stability depends on the inclination of an explosive to physical changes, occurring under the influence of different causes.

Chemical stability is characterized by the speed of change of an explosive as a result of chemical transformations, which occur in it.

§1. Chemical Stability

1. The Theory of Chemical Stability

The greatest practical value is the chemical stability of an explosive at comparatively low temperatures, which correspond to ordinary storage temperatures. The duration of storage may be very great and, if the speed or acceleration of reactions are great, then the explosive can be changed to a significant degree, and with large quantities, decomposition can even lead to detonation.

The processes distinguished, occurring at slow chemical transformation of an explosive, as shown, can be conducted on two bases:

1) primary disintegration, the speed of which is simply determined by the chemical nature of the substance and the temperature and does not depend on impurities and external conditions.

2) self-accelerated transformation.

The speed of a primary process, which at a given temperature is not able to be decreased, determines the maximum possible of the stability of an explosive. This speed in principle can be calculated if the kinetic disintegration constants are known. The speed of a primary reaction strongly depends on the temperature, and at low temperatures it usually is very small. Thus, for instance, if one considers for nitroglycerine according to Robertson in the equation of Arrenius for the constant of speed of primary monomolecular reaction

$$K = be^{-E/RT};\ B = 10^{18.64};\ E = 43{,}700 \text{ cal/mole},$$

that it is possible to calculate the half-life:

$$t_{1/2} = \frac{1}{K} \ln 2.$$

The value of K and $T_{1/2}$ at various temperatures is given in Table 3.1.

Table 3.1. The Constant of Speed K and Half-Life $T_{1/2}$ of Nitroglycerine

Temperature air degrees, C	Constant of speed K in sec^{-1}	Half-life $t_{1/2}$ in years
0	$10^{-16,34}$	$4,8 \cdot 10^{8}$
20	$10^{-13,96}$	$2 \cdot 10^{6}$
40	$10^{-10,93}$	1870
60	$10^{-9,20}$	35

Nitroglycerine as compared to many other explosives is characterized by a relatively great constant of speed of monomolecular disintegration. In spite of this, as can be seen from Table 3.1, even for nitroglycerine this speed at usual temperatures of storage is so small that it by itself cannot have practical value.

The primary process is able, however, to play an indirect role, even if inasmuch as its products evoke a self-accelerated reaction.

A basic factor, determining chemical stability, is the possibility of the flow and characteristic of self-accelerated reactions. The speed of these reactions depends on the temperature to a smaller degree than the speed of the primary reaction. Therefore, their proportion grows with lowering of the temperature. Along with this, the speed of self-accelerated reactions to a significant degree can depend, as we saw, on certain conditions of disintegration.

In principle, knowing the speed of secondary self-accelerated reactions at high temperatures, it would be possible to calculate its magnitude and for low temperatures. However, such a calculation is practically not realized because the characteristic of secondary reactions and the influence on them by different factors quantitatively still insufficiently have been studied. Due to this the speed of secondary reactions during storage of different explosions are usually judged on the basis of comparative experimental determination of the total disintegration rate at temperatures, possibly close to the temperatures of storage.

In distinction from a primary reaction it is possible to influence the speed of secondary self-accelerated reactions. This is attained by purification of explosives from impurities, promoting development of secondary reactions, and the introduction into the explosive of such substances, which join products accelerating disintegration.

There are known and widely used in practice two methods of guaranteeing maximum stability of nitroesters. One of these methods consists of thorough purification of the nitroester from residues of the acid mixture, used during nitration, and also from unstable impurities, which can be formed during nitration as a result of side reactions. Unstable impurities, being decomposed faster of nitroester, form nitrogen oxides, which with water give nitric and nitrous acid. These acids, just as residues of the nitrating mixture, not washed from the nitroester, accelerate its disintegration, especially, if in nitroester water assists and hydrolysis is possible.

The second method of guaranteeing stability, supplementing the first, consists of an addition to the explosive of small quantities of stabilizers — such substances as (diphenylamin, alkyl-aryl-urea, and others), which are in a state to react rapidly with the formed nitrogen oxides and, connecting them, preventing the formation of acids. In this case accelerated decomposition does not set in as long as the stabilizer is not exhausted.

As a result of freeing explosives from impurities, which promote autoacceleration of disintegration, and removal with the help of stabilizers of those products of disintegration, which this acceleration evokes, the total disintegration rate may be decreased to a minimum. This minimum corresponds to the speed of the primary monomolecular reaction at the given temperature.

2. The General Characteristic of Methods of Experimental Determination of Chemical Stability

In view of the complicated dependency of the total disintegration rate of an explosive on the temperature for a characteristic of stability, it would be desirable to determine this speed directly at low temperatures. However, such determination is hampered by the fact that the speed of transformation at low temperatures is extremely small and to measure it fast is difficult. Therefore, for establishment of stability, usually the disintegration rate at heightened temperatures, at which disintegration is determined, occurs faster. Furthermore, for reducing the time the test are limited by determination of speed only at the beginning stage of transformation. By the temperature dependency of speed it is possible by means of extrapolation to calculate its value at any interesting research temperature.

The authenticity of such a method of appraisal of stability is essentially lowered by two circumstances. As noted above, the change of temperature of transformation can be accompanied by a change of not only speed, but also the direction of the reaction. Therefore, the simplest method of extrapolation, based on the usual dependency of the constant of speed on the temperature $K = Be^{-E/RT}$, turns out to be little reliable, especially in those cases when on large changes of temperature are extrapolated.

The second weak point of the appraisal of stability on initial speed of transformation is the fact that the character of its further flow is not considered. At the same time for various explosives transformation can be strongly distinguished, as we saw on the example of nitroglycerine and nitramine, in the first place by the magnitude of autacceleration and by the influence on this acceleration of certain conditions of disintegration and impurities. The greater these distinctions, the more difficult during comparison of initial speeds of transformation it is to judge about its further flow, in particular, about the relationship of maximum speeds and times of their achievement.

In virtue of these causes, for reliable determination of stability of explosives it is necessary to know the kinetics of the transformation to all its extent or, at least, to a significant part of it and besides at temperatures and conditions, possibly close to temperatures, which take place in practice. This especially pertains to explosives new in chemical structure, the type of disintegration which is unknown. Knowing the speed of transformation as a function of time, one can determine what part of a substance will be decomposed during the time, during which the explosive is stored, and to establish, when the explosive will become unfit. It is also essential, so that during storage such high speeds of transformation, at which explosion can appear by the thermal mechanism are not attained.

Unfortunately, to realize such determination of stability is very complicated, since a test at low temperatures require large time. Therefore, in conditions of production and application usually are satisfied by fast, but less reliable samples, characterizing quantitatively, and sometimes even only qualitatively initial speed of the chemical transformation of the explosive.

For increasing the reliability of a test they are trying as much as possible to lower the temperature, as which it is conducted, nearing it to temperatures of storage. However, here we meet with the already noted above difficulty. The quantity of the substance, decomposed after a small interval of time, by which it is possible to judge the disintegration rate, becomes very small, with difficulty accessible for measurement and characterizes only the most initial stage of disintegration.

In virtue of the presented causes, in the practice of determination of stability, there appear opposite tendencies:

1) carrying out of an experiment at a high temperature, far from usual temperature of storage and use of an explosive that allows comparatively fast to attain significant degrees of disintegration,

which are corresponding practically dangerous, for instance a test for detonation or for the appearance of brown vapors during heating of nitroesters at 132°C:

2) use of a low temperature, for which for guaranteeing a small duration of test very sensitive methods caused, allowing to reveal insignificant quantities of products of disintegration, for instance a test of nitroesters at 65-80°C on the formation of nitrogen oxides, revealed iodized starch paper.

In both given examples the test essentially is qualitative or, more exact, semiquantitative, since although we also determine the time of achievement of that or another degree of disintegration, this degree is determined qualitatively and in most cases subjectively, by the eye — by the change of color of reagent paper or a gas above the substance and so forth.

This deficiency in a known measure is removed in those methods, where the degree of disintegration is determined by quantitative physical or chemical-analytic methods (for instance, the described below sample on the separations of nitrogen oxides sometimes called the Bergman-Yunk sample).

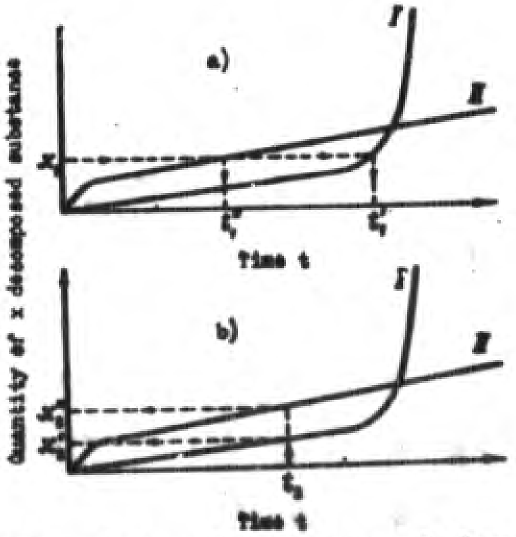

Fig. 3.1. Two types of development of the disintegration of an explosive in time.

Existing methods of determination of chemical stability can be divided into two groups. In methods of the first group stability is characterized only by one point of a curve, depicting the occurrence of the reaction in time. Besides they determine either the time t_1, necessary for formation of a definite quantity of x_1 products of disintegration (Fig. 3.1a) or a quantity of x_2 products of disintegration, formed on the expiration of a definite time t_2 (Fig. 3.1b). In methods of the second group the flow of disintegration from its beginning to achievement of a certain more or less significant degree of decomposition are traced and quantitatively part of a curve is obtained, depicting occurrence of the reaction in time.

The majority of tests for stability applied in practice as semi-quantitative (sample with reagent papers), as well as quantitative (test for separation of nitrogen oxides, sample in a Dyuar container and others) belong to the first group. This is determined in the first place by the great simplicity of such methods. At the same time methods of the first group have essential deficiencies, especially when there is talk about determination of the most initial steps of disintegration. In this case usually it is impossible to establish the origin of products of disintegration — whether they were obtained from the disintegrations of an explosive or from disintegration of unstable impurities, and also to judge about their influence on the further flow of disintegration and about how far it will be practically dangerous.

For illustration of that said Fig. 3.1 gives the practically possible curves of the flow of disintegration of two explosives. If we define the quantity of the substance decomposed after a certain interval of time t_2, as stability, we will come to the conclusion that substance I is more stable, where the real relationship of stability, as further movement of disintegration shows, is the opposite.

Therefore, methods of the second group are much more reliable. However, quantitative study of the movement of disintegration is linked with significant difficulties. The basis of them consists in the fact that it is reliably necessary to establish the quantity of the disintegrating substance. Chemical-analytical methods in reference to a majority of explosives, constituting more or less complicated organic compounds, have not been developed. During quantitative determination of any sort of gases of disintegration there is no confidence that the quantity of this gas is a measure of the quantity of the decomposed substance. In exactly the same way this confidence is lacking during the use of a general quantity of forming gases as a characteristic of the flow of disintegration, as this is done in manometric methods.

During change of conditions of disintegration (temperature, stage of disintegration), as we saw, the composition of gases can be changed, but consequently, the reaction producing them can be also changed. Therefore, the total quantity of gases, being the result of a very complicated total reactions, can not always serve as a simple kinetic characteristic of the flow of disintegration. If, nevertheless, the quantity of gases, forming after a definite time at a given temperature, used widely as a measure of chemical stability of explosives not only in practice, but also during scientific research, then this is explained quite simply also by the universality of method, since all explosives during decomposition form gases.

It is necessary to add that usually by the same considerations of simplification of the method, the quantity of gases are determined by an increase of their pressure, conducting an experiment at a constant volume of the container, this, undoubtedly, is worse than volume determination, since a change of pressure in many cases renders influence on the disintegration rate due to autocatalysis by gaseous products of the reaction or reaction of them with the condensed substance; in practice decomposition usually flows without an increase of pressure.

Up to now, speaking of the chemical transformation of explosives in connection with its stability, we considered the disintegration of explosives inform. However, chemical transformations of explosives during storage are not certainly necessarily connected with the disintegration of its molecule. They can constitute other types of reactions as well, for instance, the reaction of exchange decomposition.

Thus, in preservative ammonites, containing sodium chloride along with ammonium nitrate, interaction of these salts occurs according to the equation

$$NH_4NO_3 + NaCl \rightleftarrows NH_4Cl + NaNO_3,$$

especially fast, if the explosives contain moisture. As a result of this, ammonium nitrate is partially turned into chlorous ammonium which leads to a change of the explosive properties of ammonite and, in particular, its safety properties.

In conclusion we add that the question of chemical stability is especially urgent in the case of smokeless powders. This is caused by a series of causes. First, the basic component parts of these powders – nitrocellulose and liquid nitrates of polyatomic alcohols – by their own chemical nature possess limited stability, where nitrocellulose as a high-molecular solid unmelted substance of natural origin with labor yields to purification from impurities, lowering its stability. Secondly, the character of disintegration of nitroesters is sharply self-accelerated, especially at low temperatures, so that decomposition of large masses of powders can lead to self-ignition and detonation. In the beginning of wide use of smokeless powders a number of such cases took place (the catastrophe on battleships of the French fleet "Iyena" and Liberte" and others). Third, smokeless powders have a military purpose, therefore, they will be subject to prolonged storage in the form of mobilization reserve. Finally, from powders (in distinction to explosives) strict ballistic constancy of action is required, decomposition can be significantly reflected on those properties of the powder, which determine this action, in the first place on the burning rate.

Methods of determination of the chemical stability of powders have been suggested and many have been used. This is combined with the large value of the question and with the complexity of phenomena, determining stability. Because of the insufficient reliability of the existing method, new, seeming more reliable methods were developed. At present there are degrees of suggested methods, but not one of them can be considered fully satisfactory, universal and indisputable.

In view of the lack of a single reliable method, usually in responsible cases not one, but several methods of a test is used and by the aggregate of the results a judgement about stability is made.

A description and analysis of all methods does not enter in our problem, therefore, below will be considered only certain of the most wide-spread samples on stability.

3. Basic Methods (Sample) for Determination of Chemical Stability

1. A test for detonation is characterized by the highest, as compared to others, temperature of heating of the explosive and therefore, small duration. This sample is executed in two varieties. By the first variant, a small batch of explosives (0.1-0.5 g) is heated in a test tube, placed in a bath with a liquid, temperature of

which increases with a definite speed. The temperature of the bath, at which detonation occurs is determined. By the second variant, a batch of explosives is held at a constant temperature and the delay time of detonation flash is determined, sometimes at several temperatures.

The results of this test make it possible to judge stability only in the case when the temperature of the detonation or delay time of it turns out to be less than for a pure, known stable (standard) substance. This means that the tested sample possesses lower stability. If however, a distinction during determination of temperature of the detonation is not obtained, then this still does not make it possible to conclude that the stability of the tested and standard substances are identical.

During a test of various explosives a sample can reveal only sharp distinctions in stability.

2. The test for the appearance of brown vapors is also characterized by a high testing temperature; 132 or 135°C. Definite batch of the substance is heated in a loosely closed glass or long test tube, with a closed glass cap (Fig. 3.2), in contact with air to the appearance of visible to the eye brown vapors (nitrogen peroxide). Pyroxylin powder with a stabilizer sustain a sample at 132°C for 5-6 hours; nitroglycerine powder without a stabilizer give brown vapor in 20-30 minutes; the same powder, containing one percent centralite in not less than 30 minutes; nitroglycerine powder with three percent centralite sustains a sample for 4-6 hours.

To the deficiencies of this sample should be related its limited sensitivity and bad reproducibility of results. The sample is a poor model of condition for storage, in particular, from the high temperature of the experiment and unhermeticity of the container moisture departs from the powder; due to this its possible hydrolytic action does not occur, furthermore, if the powder contains such additions, which combine nitrogen oxides only in the presence of water, then the action of these additions will not appear. Finally, during the test of certain low-calorie powders the concentration of brown vapors grows very slowly and the color remains very weak for a long time.

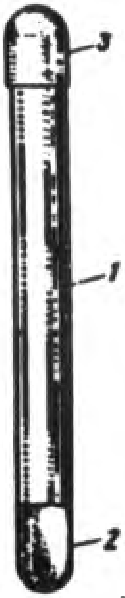

Fig. 3.2. Test tube for sample on the appearance of brown vapors. 1 — test tube; 2 — powder; 3 — glass cap.

By all of these reasons, a sample on brown vapor in its initial form at present is excluded from a number of our samples, anticipated by corresponding standards.

A variant of a sample on brown vapor is the Vlasov sample. With respect to conditions of fulfillment (dimensions of glass, batch of powder, temperature of test), this sample is analogous to the litmus sample of V'el (see below), but differs by the fact that in the cover of the glass is a hole with a diameter of 2 mm. The purpose of the hole is to ensure the possibility of removal of volatile products of disintegration, to such a degree that there is room for a repeated V'el sample.

The test on the Vlasov sample for artillery ballistic powders is produced at 115°C. With this the powder does not have to give brown vapors earlier than in 35 hours.

Mortar ballistic powder test on the Vlasov sample at 106.5°C, must be sustained for not less than 25 hours. With this temperature of the artillery ballistic powder give brown vapor in 120-160 hours.

For a test of an explosive test for brown vapor the name of a railroad sample is applied. This name was obtained in connection with the fact that in Germany substances for transports by railroads are only allowed which sustain a sample on brown vapor.

The test consists of a batch of 10 grams of dynamite or another nitrogen-containing explosive heated in a loosely closed glass in a thermostat at 75°C for 48 hours, with this brown vapors of nitrogen oxides should not appear.

3. Test for separation of nitrogen oxides (Bergman-Yunk sample) is produced at 132°C. The degree of decomposition on expiration of on the expiration of a definite interval of time is determined by methods of quantitative analysis.

A batch of pyroxylin(2 g) or powder (5 g) is heated for 2 hours in a test tube with a rubbed cork, supplied with a cap, containing water for absorption of nitrogen oxides (Fig. 3.3). After the experiment during cooling of the tube water is sucked inside the test tube. Then in the test tube water is added to a definite volume, thoroughly agitated, filtered and determined to a definite part of the filtrate quantity of combined nitrogen in the form of the NO gas volume method.* The permissible limit for pyroxylin No. 1 is considered 3.5 cm^3 of nitrogen oxide on 1 g for a 2.5 collodion and a 3 cm^3/g cotton collodion. For powders (with

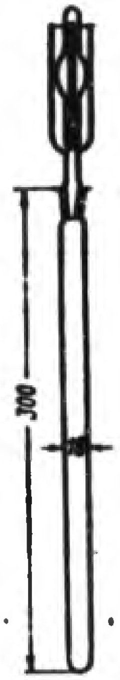

Fig. 3.3. Test tube for Bergman-Yunk sample on the separation of nitrogen oxides.

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*In an improved variant of the sample such a form of a test tube is used so that a drop of condensed water in the upper part could not fall on the hot explosive being tested, with this, the volume of the test tube is increased, so that atmospheric oxygen is sufficient for oxidation of nitrogen oxides to NO_2, finally, determination of the mixture of nitric and nitrous acids in water is produced and by a more simple iodide data method.

continued heating for 5 hours) the quantity of nitrogen oxide is 6-7 cm^3/g (ballistic artillery powders) and 5-9 cm^3/g (mortar ballistic powders).

4. The litmus sample (V'el sample) is executed at 106.5°C rarely at 115°C and consists of heating a batch of powder, placed in a thermostat in a hermetically closed glass with standard blue litmus paper (Fig. 3.4). Observation of a change of color of the paper is conducted through a glass window of the thermostat every half hour. Usually in the thermostat there are several glasses with samples. For guaranteeing of identical temperature of all samples tiers, in a hole of which the glasses are inserted is rotated. Earlier this sample was used also for a pyroxylin test. Satisfactory by stability pyroxylin gave a violet coloring no earlier than in 2 hours, pink in 4-5 hours, red in 6-7 hours. Upon the expiration of seven hours the test ceased. The ballistic artillery and mortar powders sustained the test by this sample for not less than 7 hours.

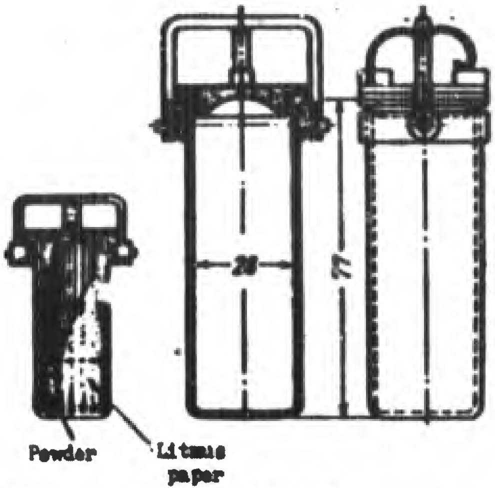

Fig. 3.4. Glass for litmus sample with batch of powder and indicator paper.

Besides the described simple litmus sample, for testing powders still so-called repeated litmus sample at one hour are used. Its peculiarity is the consecutive use during a number of days of batches of the substance, subjected to testing the day before. The test continues until reddening of the litmus paper does not decrease one hour. The total hours, obtained during all the tests, serves as a measure of the stability of the powder.

A stable powder is attained during repeated litmus sampling the following times: ballistite artillery 130-180 hours; pyroxylin — not less than 90-110 hours, depending on the brand.

With an abbreviated variant of repeated litmus sample the testing is not brought to one hour, and limited to ten repeated tests.* Ballistite artillery powder by the repeated abbreviated litmus sample must give a total time not less than 65 hours, ballistite mortar — not less than 30 hours; pyroxylin artillery — not less than 60 hours; cellular pyroxylins — not more than 50 hours.

The litmus sample at present is our basis for testing stability of pyroxylin powders, as well as powders of the ballistite type. Its use is complicated by a series of peculiarities of powders in a difficult volatile solvent: the appearance of red coloring of paper occurs very gradually and unsharply, the grains or particles of the powder are inclined to sticking together at increased temperatures by measure of decomposition, the distillation of the volatile sometimes colored component parts in the greater part of the container hampers the observation of the change of color of the paper and others.

5. The sample of Vill consists of heating the sample of the tested substance in a butyric bath, having a temperature of 135°C, with continuous transmission of carbon dioxide, consequently, during removal of the volatile products of disintegration (Fig. 3.5). Carbon dioxide with the products of disintegration pass then over the heated reduced copper. Nitrogen oxides are reduced with this to elementary nitrogen. After transmission on the heated copper oxide (oxidized CO and so forth to CO_2), the gases gather over the alkali solution, which absorbs the carbon dioxide. The volume of nitrogen is periodically measured, and it serves as a measure of the quantity of the

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*If the time of coloring of the litmus paper is reduced to one hour before the tenth day, then the test on this is finished.

reacting substance.

6. Test for loss in weight in diverse variants, differing mainly by the temperature of the experiment (from 115 to 50°, usually 95 or 75°), consists of heating a batch of powder in a thermostat in an open glass for weighing. Through definite intervals of time (for instance, through 10 twenty-four hour periods at 75°, through twenty-four hours at 95°) the powder is weighed and a graph is drawn, deferring time along the axis of the abscissas and the decrease of weight in percent along the axis of the ordinates. The test finished during the approach of a sharp increase of loss in weight, expressed in the distinct change of slope of the curve (Fig. 3.6). The duration of heating serves as a measure of stability. On the variant of the sample at which the batch of powder is heated in a container, transmitted with an atmosphere by a capillary with a diameter of one mm, at a temperature of 95° this time should be no less than 8-10 twenty-four hour periods (depending on the brand of powder).

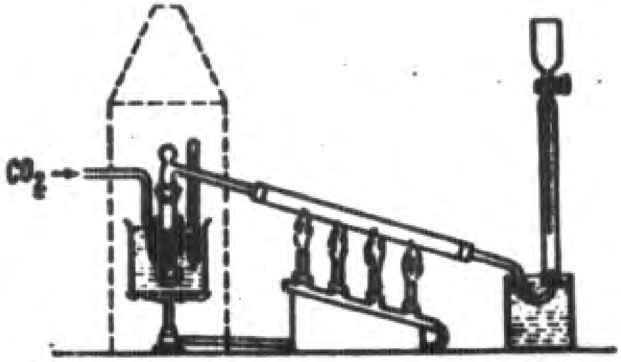

Fig. 3.5. Diagram of the test on the Vill sample.

Fig. 3.6. Curve of loss in weight of powder during heating.

7. The Obermuller sample belongs to the number of manometric samples at which the mercury manometer directly measures the pressure of the gaseous products of decomposition of the batch of explosives (2 g), decomposed in constant volume. The instrument is shown in Fig. 3.7. The reaction container before the experiment is pumped out.

A curve, depicting the pressure of gaseous products of decomposition as a function of time, serves as the characteristic of stability.

A vacuum sample, used in the United States, on conditions of carrying out an experiment is close to the Obermuller sample. Samples on 5 g of explosive (for a very sensitive or powerful explosive use one g and a smaller heating time) heated in parallels at a temperature of 100, 120, and 150° for 40 hours in pumped out (residual pressure 5 mm) test tubes united with capillary mercury manometers. The quantity of separating gases and the change of this quantity depending on the temperature characterize the stability of the explosive. If the quantity of separating gases in the course of the experiment attains 11 cm^3, then the test is stopped. Data, obtained with such a test for a number of explosives, is given in Table 3.2.

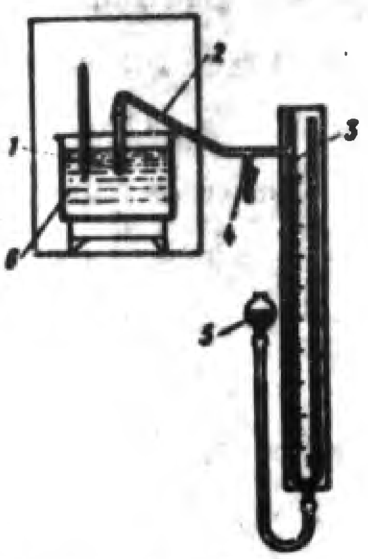

Fig. 3.7. Instrument for the Obermuller sample. 1 — glass test tube with slide, 2 — bent tube with slide, 3 — mercury manometer, 4 — vacuum-pump cock, 5 — equalizing bulb, 6 — bath.

The sample of Talian also is a modification of the Obermuller sample. The basic distinction of the Talian samples is that the emptying of the container before the experiment is not accomplished; furthermore, the instrument has a paraffin lock, preventing diffusion of gaseous products of decomposition to cold parts of the measuring system (Fig. 3.8). Usually decomposition is conducted up to a pressure of 100 mm of the mercury column. The time, necessary for that, is considered as the measure of stability.

A variant of the manometric sample was developed by Khaydom,

Table 3.2. The Characteristic of Chemical Stability of Certain Explosives by Vacuum Sample

Explosive	Weight in g	Indices of chemical stability by vacuum sample					
		cm^3	hrs.	cm^3	hrs	cm^3	hrs
		100° C		120° C		180° C	
Ammonium nitrate	5.0	—	—	0,3	40	0,3	40
Ethylenedinitramine	5.0	0,5	40	1,5	40	11	24
Nitroguanidine	5,0	0,4	40	0,5	40	—	—
Diethyleneglycoldinitrate	1,0	0,8	40	1,3	8	—	—
Nitroglycerine	1,0	11	16	—	—	—	—
Erythritoltetranitrate	1,0	11	16	—	—	—	—
Tetranitrate	5,0	0,5	40	11	40	—	—
Dipentaerythritolhexanitrate	5,0	3,7	40	11	16	...	—
Mannitolhexanitrate	1,0	11	16	—	—	—	—
Nitrocellulose (13.3% N)	5,0	0,9	24	11	16	—	—
Hexogene	5,0	0,7	40	0,9	40	2,5	40
Octogene	5,0	—	—	0,4	40	0,6	40
Trotyl	5,0	0,1	40	0,4	40	0,7	40
Picric acid	5,0	0,2	40	0,5	40	—	—
Ammonium Picrate	5,0	0,2	40	0,4	40	0,4	40
Tetryl	5,0	0,3	40	1,0	40	11	12
Hexyl	5,0	—	—	0,4	40	—	—

Beyrum, Hyde, Baker and Ditman. The peculiarity of the method is the use of a low (75°C) temperature of heating. In order to obtain with this in the flow not too large an interval of time of change of the pressure, sufficient for exact measurement, use a container and manometric tube united with it of a small volume, but the batch of the tested explosive — large, 42 g. Reading the pressure, as a rule, is done daily. The characteristic of stability is determined after several weeks. Fig. 3.9 shows curves, obtained during a test of nitrocellulose and powder by this method, and Fig. 3.10 — tetranitrate and hexogene. In the case of nitrocellulose (curve 1 in Fig. 3.9) at first a certain lowering of pressure is observed, obviously, at the expense of the reaction of the explosive with atmospheric oxygen, then a section of slow change of

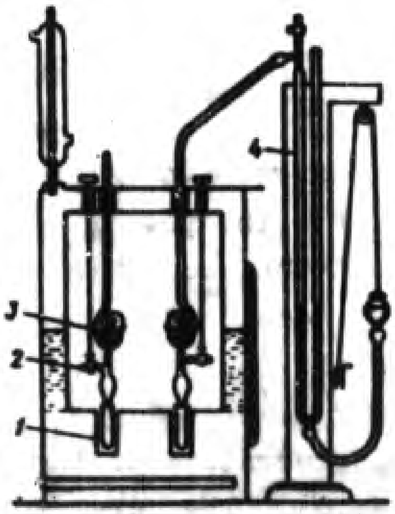

Fig. 3.8. Instrument for Talian sample. 1 — test tube for explosive with slide, 2 — cock for exit of air during heating, 3 — paraffin lock, 4 — mercury manometer.

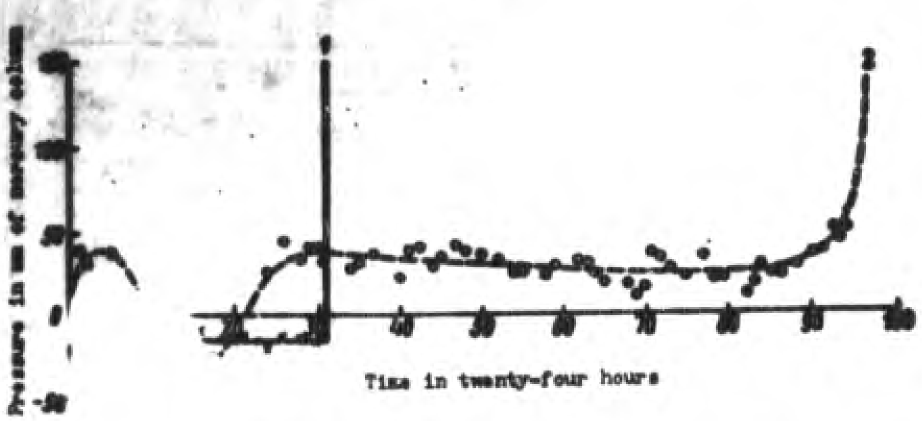

Fig.).9. Change of pressure in time during test of nitrocellulose (1) and pyroxylin powder (2) by Hyde, Baker and Ditmar.

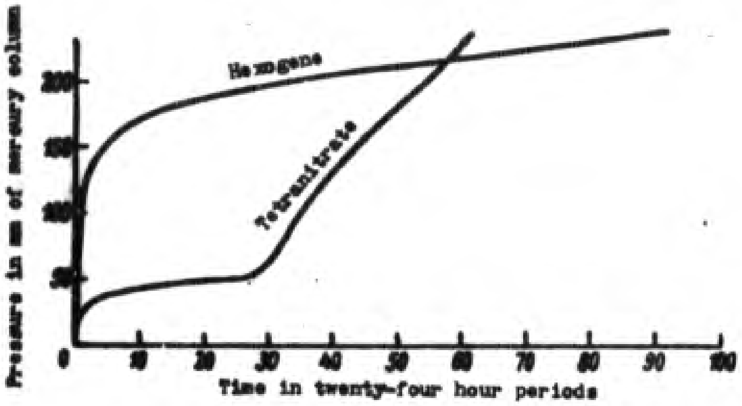

Fig. 3.10. Change of pressure in time during testing of tetranitrate and hexogene.

pressure occurs, after which a sharp acceleration occurs, typical for nitric acid esters of alcohols and carbohydrates. For the powder (curve 2) the beginning of the accelerated decomposition occurs later, since the contents contained in it are stabilized. Acceleration of decomposition coincides with the appearance of visible to the eye, brown vapors.

A large stability of tetranitrate at the low temperature of the test is confirmed by these experiments (see Fig. 3.10). The curve for hexogene (see Fig. 3.10) goes high, but acceleration within the limits of 100 days is not observed. The gases formed are, apparently, the result of decomposition of impurities, not accelerating the disintegration of the basic substance. Nitro compounds of aromatic hydrocarbons give an insignificant yield of gases, in the case of trotyl after 100 days the pressure attains a total of 20 mm of the mercury column.

8. The definition of the concentration of hydrogen ions is comparatively a new sample, used in those cases, when during decomposition acid products are formed. The test is executed by the following form.

Nine samples of explosives are placed in special test tubes in a thermostat, having an increased temperature (usually 110°C). Every hour after the beginning of heating one test tube is removed. After 30 minutes of cooling in the air the contents of the test tube are agitated with distilled water, in which after bringing to the mark the quantity of acid products of decomposition on concentration of hydrogen ions is determined. The measure of stability is the change of pH. The author of the sample, Ganzen, recommends for the characteristic of a stable powder to use the total pH of all nine samples, which for a stable powder should be not less than 30.

9. Iodized starch sample (sample of Abel) is one of the oldest tests for stability, it is used mainly for control of production of nitroglycerine and nitroglycerine explosives. The sample is based on the reaction between nitrogen oxide, formed during disintegration of the explosive in contact with air, and potassium iodine which is impregnated with starch indicator, a so-called iodized starch paper.

The batch of nitroglycerine ($3.2 \text{ g} = 2 \text{ cm}^3$) is placed in a test tube of definite dimensions. Test tube as closed by a rubber cork, through which passes a small glass rod with a platinum or glass hook. On hook a line is suspended with standard iodized starch paper. Before introduction in the test tube, the lower half of the indicator paper is moistened with a solution of glycerine in water. The tube is placed in a water bath, which is maintained at a temperature of 75°C

(Fig. 3.11). During decomposition of the nitroglycerine in these conditions nitrogen peroxide will be formed, which reacts with potassium iodine, separating free iodine, which gives with the starch on the boundary of the moistened and unmoistened parts of paper, a reddish-brown line.

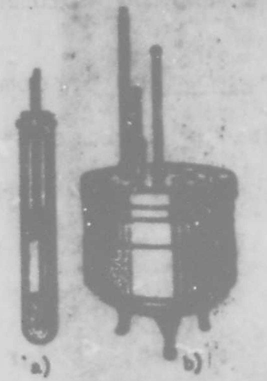

Fig. 3.11. Test tube (a) and bath (b) for test of explosive for stability by iodized starch sample.

The nitroglycerine, intended for the preparation of dynamite, is considered to sustain the test, if a line on the indicator paper appears not earlier than in 15 minutes. To the nitroglycerine, use for the manufacture of powders, are presented more rigid requirements: it should sustain a test by an iodized starch sample at 72°C for 30 minutes.

The testing of gelatin-dynamite differs by preliminary preparation, in that the bath of explosive is carefully pulverized with talc. If one were to use dynamite in the form of a solid piece, then nitrogen oxides separating inside the gelatins will be very slowly diffused through the layer of dynamite to the air and the test will show exaggerated stability. During pulverizing with talc the dynamite obtains a powdery structure, which the separated nitrogen oxides get into directly in the air and can influence on the paper. Dynamite is considered sustaining the test, if a line on the paper appears not earlier than 10 minutes.

The basic advantage of an iodized starch sample is the simplicity and speed of fulfillment. At the same time, the results of this sample are subjective enough and to a significant degree depend on the volatility and moisture content of the substance, from impurities,*

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*For instance, a sample of hexogene, the curve of test of which is by the manometric method (p. 177) testifies to the high stability, given during a test by iodized starch sample in a small time to the appearance of a line. This was conditioned by the presence of impurities, since after heating of hexogene in a certain time at 100°C the indications of iodized starch sample were sharply increased.

and also from a whole number of difficultly controlled factors (the condition of storage of the paper, weather, magnitude of the moistened part of paper, cleanness of the air with respect to oxides of nitrogen and others).

The sample of Yanov is based on the same reaction between iodine and starch, accompanied by blue coloring, intended for a fast appraisal of the degree of decomposition of powder. The sample is executed by following the form.

To a batch of 20 grams of powder 50 ml of distilled water is added and the container with powder and water is placed for a definite time (from 5 to 15 minutes depending on the dimensions of the particles) in a bath with boiling water. After the heated contents are agitated then 10 ml of it are placed in a test tube, solutions of potassium iodine and starch are added and in 5 minutes a change of color is observed: coloring of the contents of the test tube in blue color indicates the unstableness of the powder.

10. Sample by heating of a bath of powder. The samples used in England by heating a bath of powder (50 g) in a Dyuar container at 80°C occupies a special position by method of the appraisal of the movement of decomposition. A thermometer is inserted in the container, the ball of which is placed in the middle of the batch of powder. Due to the exothermic nature of the reaction of decomposition, the temperature of the powder rises. When the increase of temperature attains 2°, the test stops; the time of heating serves as a measure of the stability of the powder. Good cordite sustains this sample for 500-600 hours.

11. Definition of time of complete fusion. For solid explosives, decomposed with noticeable speed near the temperature of fusing and

forming with this condensed products of disintegration, soluble in the parent substance, American researchers offered to characterize the stability and action of stabilizing additions by time of full fusion. A sample of an explosive (almost 2 mg) was placed on a warmed table of a microscope and at definite temperatures, lying lower than the temperature of fusing, the time of full fusing (disappearance of crystals) was determined. Stabilizing additions increase this time. The more time is increased, the stronger the stabilizing action of the addition. As an example on Fig. 3.12 is given the dependency of time of full fusion as the temperature for pure methylenedinetramine (curve 1) and for methylenedinitramine with an addition of 2.6% picric acid (curve 2), which as an acid is able to stabilize the nitramine of the aliphatic group.

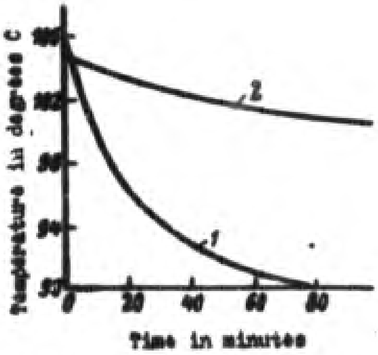

Fig. 3.12. Dependency of time of full fusion of methylenedinitramine without additions (1) and with the addition of 2.6% picric acid (2) on the temperature.

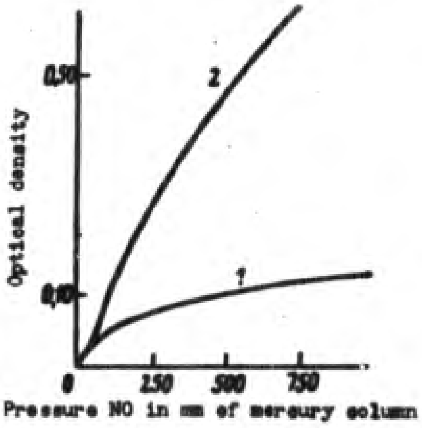

Fig. 3.13. Influence of an inert gas CO_2 on the optical density of nitrogen oxide. 1 — optical density of nitrogen oxide without additions; 2 — optical density of nitrogen oxide after addition of carbon dioxide under a pressure of one atom.

12. The sample of Lambrey, shown earlier, the essential deficiency of all tests for stability is the necessity of the use of high (as

compared to usual temperatures of storage) temperatures of the test. Hence, the understandable tendency of researchers to possible lowering of the temperature of the test. The attempt of the development of such a sample was carried out by Lambrey, who used for the determination of stability the method suggested by him to determine optical density of nitrogen oxide at very low pressures (up to 0.015 mm of the mercury column). Furthermore, Lambrey established that the optical density of nitrogen oxide strongly increases during addition of large quantities of inert gases, for instance, carbon dioxide (Fig. 3.13). Thanks to this phenomenon it is possible with great accuracy to measure insignificant concentrations of nitrogen oxide.

For carrying out of the sample of Lambrey an explosive in a quantity near 8.5 g was placed in the tube (Fig. 3.14), which the flat side is united with a tube two 60 mm in length with quartz apertures 3. The compound of tubes and the connection of apertures is hermetically sealed with the help of picein. The cock 4 closes the entire system. Before the test the system was pumped for 120 hours for removal of gases, adsorbed in significant quantity, especially in the case of pyroxylin, and particles of explosives. Then cock 4 was closed and partly placed in the thermostat for the necessary time, upon the expiration of which the absorption spectrum of gases was photographed, which were contained in the tube 2, preliminarily adding carbon dioxide when needed. The nitrocellulose obtained for different samples during three temperatures curves are shown in Fig. 3.15.

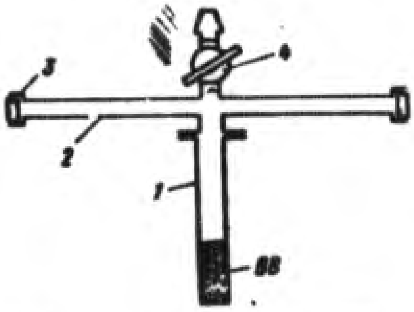

Fig. 3.14. Instrument for the test of stability by Lambrey. 1, 2 – tube, 3 – quartz apertures, 4 – cock.

From the curves it is clear that at first the formation of nitrogen oxide occurs comparatively very fast, and then is delayed. The initial rapid decomposition Lambrey connects with the presence in the nitrocellulose of insignificant impurities (full decomposition of these impurities gives 0.435 milligram NO per one kg of nitrocellulose). It is possible, however, that the initial rapid yield of nitrogen oxide occurs at the expense of the products of decomposition, absorbed by the nitrocellulose. A decomposition, flowing subsequently, constitutes in the opinion of Lambrey, the decomposition of the nitrocellulose itself. At 43°C the quantity of formed nitrogen oxide is of this order of 0.65 mkg per day on one kg of nitrocellulose which corresponds to a disintegration of $2.4 \cdot 10^{-9}$ of the substance. For the disintegration of one percent nitrocellulose 1140 years will be required with such a speed. For tetranitrate the speed of decomposition at 43°C is at the limits of the possibility of measurement.

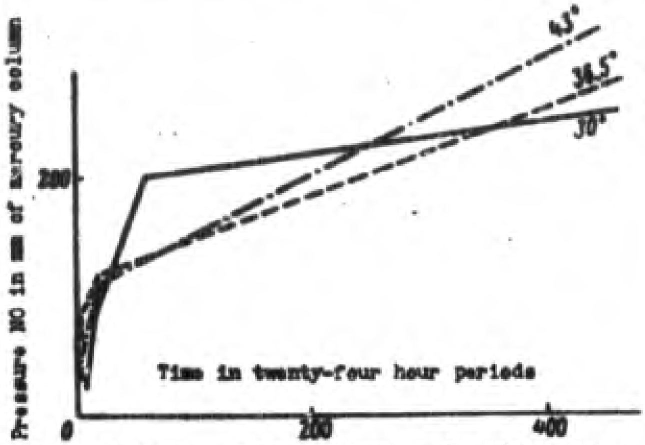

Fig. 3.15. Formation of nitrogen oxide during heating of nitrocellulose according to Lambrey.

Results of tests by the Lambrey sample, as he himself indicates, cannot be considered fully reliable, since during determination of such small quantities of nitrogen oxides any side factors may play a large role, as for example absorption of nitrogen oxide by picein and the lubricant of the cock, absorption of them by pyroxylin, etc.

An indubitable interest for the study of the stability of explosives is the use of radiochemical methods, which give possibility with great accuracy to determine insignificant quantities of the substance.

Use of such methods make it possible to conduct determination of the disintegration rate for an explosive at such low temperatures, at which disintegration cannot be traced by other used up to now methods.

The definition of stability by radiochemical methods can in principle be carried out, preparing a corresponding explosive, for instance, nitroester, marked by long-lived radiocarbon C^{14}, the activity of such an explosive will be of the $2 \cdot 10^8$ impulses/min g. If during disintegration of the explosive, carbon containing lightly volatile intermediate products are formed, then after their separation and burning carbon dioxide $C^{14}O_2$ will be obtained, which is easily transferred into barium carbonate $BaC^{14}O_3$. The activity of the carbonate may be determined with the help of a window counter. One mkg of the substance will possess an activity of the order of 200 impulses per minute. The counter allows reliably to determine 20 times smaller activity. The speed of thermal disintegration of nitroglycerine, calculated by means of extrapolation, constitutes, as we saw, at 40° about one microgram per gram in twenty-four hours and may be accessible to measurement after comparatively short periods.

Radiocarbon may also be introduced in a stabilizer of a type of centralite, which during reaction with products of the disintegration of an explosive will form carbon dioxide $C^{14}O_2$; the speed of its formation will in such a case as an index of the disintegration rate of the explosive.

§2. Physical Stability

Physical stability is characterized by the inclination of the explosive to physical changes, spontaneous or occurring under the influence of external causes. The nature and the mechanism of these changes for various explosives can be different. Let us give several examples.

Oxyliquits physically are unstable due to rapid evaporation of the liquid oxygen contained in them.

Black powder, containing water-soluble potassium nitrate, is unstable with respect to water.

Nitroglycerine powder at very low temperatures becomes fragile; this leads to cracking or splitting of the powder elements during a shot, and as a result, to a sharp increase of pressure, sometimes provoking the breaking of the barrel of the weapon or chamber of a rocket missile.

Cartridges of reagent powers of large dimensions also have limited physical stability; during prolonged storage they are inclined to use formation of cracks; this entails an irregular increase of the surface of burning, and correspondingly, pressure during a shot.

The physical stability of pyroxylin powders is limited from the possibility of evaporation of residual volatile solvent and moisture which leads to an increase of the burning rate and maximum pressure during a shot. Since pyroxylin powder possess a noticeable hygroscopicity, it can not only issue moisture, but also to absorb it at heightened atmospheric humidity. In order to decrease the oscillation of humidity and, combined with this, oscillation of ballistic properties of pyroxylin powders, attempts are being made to reduce their hygroscopicity by means of the introduction of special additions and to store the powder in a hermetic sealing.

The explosion of charges, prepared from trotyl with a low fusion temperature, can during storage separate fusible eutectic alloys in the form of an oil-like liquid. During flowing of the liquid in a charge an emptiness is formed that decreases its stability to concussion during firing. Furthermore, an explosive liquid can get in a thread of the housing and also promote premature breaks. Therefore, especially in those cases, when ammunition is intended for prolonged storage, trotyl or another explosive of high cleanness is used.

We will not remain on specific methods of determination of different forms of physical stability, but will consider more specifically only the physical stability of ammonites — the basic class of an explosive mixture of industrial and military purpose.

1. Physical Stability of Ammonites

Ammonites possess limited physical stability. They are inclined to caking and moistening during contact with water in the form of vapors or in liquid-drop state. Caking and moistening of ammonite, frequently occurring already after a short storage, worsens their explosive properties (the ability to transmission of detonation at a distance, receptivity to detonation) and lead to an increase of the quantity of poisonous gases, forming during the explosion. Compressed ammonite frequently arrives in such a state of full looseness that it is impossible anew to turn into powder by the usual kneading in hands and crushing and recartridging are required. However, even in this case, usually initial indices of the explosive properties are not completely restored .

The causes and consequence of caking of ammonite and methods of preventing it

During storage of powdery ammonite there is spontaneous enlargement and agglomeration of crystals of the oxidizer, leading to a decrease of their total surface. In the presence of moisture this process goes much faster than in a dry substance. It is possible that the change of character of pores also plays a role, some of them become closed. This change of the physical structure of the powdery explosive leads to impairment of its explosive properties. The effective surface of burning of particles during detonation is decreased and, possibly, the penetration of gases from the zone of reaction to the unreacting substance is hampered.

Basic factors, favoring caking, are the moistening of ammonium nitrate and subsequent drying, and also pressing of the substance.

The impairment of explosive properties during storage was observed also for mixtures on the basis of other water-soluble oxidizers. Thus, Vandoni observed the loss of the ability of transmission of detonation during storage of explosive P ammonium perchlorate, sodium saltpeter and paraffin, in spite of the presence of a paraffinized shell of ammunition, the explosive was moistened somewhat and crystals of salts were enlarged — the portion of particles, passing through a sieve with definite mesh dimensions, decreased from 35 to 11 percent.

It is known, that the greatest caking is possessed by materials, well dissolved in water. The moisture absorbed by such a product will form a film of a saturated solution around every particle. During drying, and for certain substances, with a decrease of temperature, from the solution new small crystals will separate, connecting among themselves earlier free particles in the durable conglomerate. Pressing promotes caking, since it decreases the intervals between particles of the hydrophilic substance, increases the surface of their contact and facilitates cohesion of particles during drying. By this last cause, a fine-grained substance is compressed stronger than a coarse-grained.

Inasmuch as caking promotes alternating of drying and moistening, then to the largest measure those salts are inclined to caking, the hygroscopic point* of which is close to the usual humidity of the atmosphere in the given site. This condition for climate of the central part of our country is executed for ammonium nitrate, the hygroscopic point of which during 20° is equal to 67 percent.

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*The hygroscopic point of a substance is called the relation of the elasticity of vapors above its saturated solution to the elasticity of vapors of water with the same temperature.

By lowering the moisture it is possible to lower and compress. Decreases of moisture can be attained by covering paper shells of ammunition with polyvinyl chloride or another difficulty permeable for moisture lacquer, and also the use of shells from plastic, which does not pass water vapor (polyethylene, polyvinyl chloride and others). A radical, but difficult to realize method of preventing the moistening of ammonite is the supporting of a small atmospheric humidity in the location, underlying the hygroscopic point of ammonium nitrate.

An active method of lowering the compactness of ammonite, besides preventing moistening, is the introduction in their composition of small quantities of certain substances: stearates of calcium, zinc, and especially iron, dyes – fuchsin and amaranth, some aliphatic amines, organic fibrous substances and others. The action of certain of these additions is combined with their influence on the structure of small crystals of the saltpeter, falling from the solution. In particular, the presence of fuchsin permits that the separated laminar small crystals are very fragile and forming agglomerates or particles of ammonium nitrate turn out to be very nondurable. A negative property of stearates is their ability to lower strongly the transmission of detonation by distance and critical density.

Stability of ammonite in relation to liquid water

Soaking an explosive in water strongly hampers conducting of blastings in irrigated conditions, since during the time from the beginning of loading the blast hole (falit) to the moment of explosion the ammunition is moistened to such a degree that incomplete explosions occur, accompanied by the formation of a heightened quantity of poisonous gases, or even rejections.

From native industrial explosives the most waterproof are 62%

gelatin-dynamite, dinaphthalite No. 1, ammonites, prepared on so-called ferric ammonium nitrate, waterproof ammonal and ammonite V-3. The waterproofness of dynamite is caused by its dense gelatinous structure in combination with a very small solubility of nitroglycerine in water, the waterproofness of ammonite has another physical basis.

The waterproofness of a powder substance, containing hydrophilic particles perhaps is attained by the creation in it of a hydrophobic mesh — a space mesh of capillaries, the wall of which consist of a film of a hydrophobic substance. If such a mesh consists of a hydrophilic substance, then water is pulled into the capillaries; in hydrophobic capillaries the force of surface tension in the zone of contact of their wall and water prevent its entry into the capillary and for surmounting these forces is corresponding external excess pressure is required. Hydrophobic mesh may be obtained by two ways: by covering hydrophilic particles by a film of fusible hydrophobic substance or powdering of these particles by thin-crushed solid hydrophobic substance. On this latter the mechanism is based, in particular, on the waterproofness of ammonite, containing stearates. Powdering of particles of ammonium nitrate by a thin powder of stearate, hampering the penetration of water in capillaries, formed by pores of powder, leads to slow moisture content of this composition.

If the hydrophobic nature of ammonite is produced by heaping particles of ammonium nitrate of a non-wettable water substance like paraffin on the surface, stearic acid or asphaltite, then such a substance should possess high viscosity, in order to be durably retained on the surface of the solid body and not to be displaced by water.

Earlier it was considered that the waterproofness of dinaphthalite depends also on its granular structure, obtainable by means of crushing treatment of the composition. Research of Voronov has determined that granulating of ammonite is a measure only against caking. Crushing treatment of the mixture gives waterproofness to dinaphthalite No. 1 because it ensures exclusively thin crushing of the hydrophobic component and formation of a small non-wettable mesh from technical dinitronapthalene. For guaranteeing the waterproofness certainly careful "rubbing" of a hydrophobic component on the surface of particles of ammonium nitrate, which is attained during crushing treatment.

Finally, waterproofness of ammonite may be attained by the introduction in its composition of impurities, swelling during absorption of water and hampering due to this its penetration in the depth of the cartridge.

A test for waterproofness is produced by means of the endurance of ammunition of ammonite by weight of 200 g for one hour in water in a vertical position where the height of the column of water above the upper face of the cartridge should constitute one m. The ammunition extracted from water is tested for transmission of detonation; for a waterproof explosive, so that a detonation is transmitted the distance should not be significantly less than the passage in water, and in any case not less than 2 cm. The degree of soaking can be estimated also externally on an explosive by cutting ammunition.

Physical changes of charges of ammonite in ammunition

Ammonites possess a limited physical stability not only in powder form at a small density (as they are used in industrial explosive matter), but also in the form of charges of significant density in ammunition.

During storage of ammunition, equipped with ammatol* by a method of pressing, to a large or small degree shrinkage is observed, and sometimes the growth of the charge also. The development of both of these phenomena depends on the technology of equipment and conditions of storage.

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*In military technology ammonite on the basis of trotyl is called ammatol.

The basic cause of shrinkage of ammatol pressed charges is spontaneous adhesion and enlargement of crystals ammonium nitrate, accompanied by a decrease of the volume of the charge similar as this occurs during caking of industrial ammonite. Enlargement of crystals promotes heightened humidity of ammatol and transitions of ammonium nitrate from one modification to another; shrinkage becomes easier, if ammatol during pressing has a temperature higher than 32°C; a small density of charges also favors shrinkage.

If during storage of the ammunition the temperature frequently rises higher than 32°C, then a growth of the charges is observed since transition through the given temperature leads to modificational transformations of ammonium nitrate, combined with an increase of volume.

Moistening ammatol charges is undesirable not only because it promotes shrinkage, but also because it decreases their susceptibility to detonation; furthermore, during the reaction of humid ammonium nitrate with metal of the housing of the ammunition can separate out ammonia which, reacting with trotyl, will form a compound (trotyls), possessing heightened sensitivity to thermal and mechanical influences. For an increase of stability of breaking charges, take measures to prevent the given phenomena. In particular, with equipment with ammatol usually place a cork of nonhygroscopic sheet trotyl over the charge.

CHAPTER IV

SELF-SPREADING CHEMICAL TRANSFORMATION IN EXPLOSIVE SYSTEMS (BURNING AND DETONATION OF GASEOUS AND CONDENSED EXPLOSIVE SYSTEMS)

The theory of self-spreading processes in explosive systems is developed significantly less than the theory of their slow chemical transformation, and not all regularities of these processes have strict theoretical explanations. Therefore, in this chapter we will consider in the first place experimental material. In the divisions, dedicated to the theory of propagation, will be given an explanation of those experimental rules, which at present have them.

The speed of propagation of explosive transformation is called the linear speed of its forward shift.*

In general the speed of propagation of explosive transformation is determined by two independent factors: the chemical reaction rate in front of the transformation and the speed of energy transfer of this reaction to the following layer. In certain cases the second

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*For a characteristic of self-spreading transformation mass speed is also used, equal to the product of the linear speed on the density of the substance; mass speed constitutes the quantity of the substance, reacting during the self-spreading process per unit of time per unit of area of the section of the charge. If the dimension of linear speed is Lt^{-1}, then the dimension of mass speed is $Mt^{-1} L^{-2}$.

factor becomes the predominant, and sometimes decisive value. Then we meet with that paradoxical phenomenon that with a decrease of the chemical reaction rate, for instance as a result of the addition of an inert gas to the explosive gas mixture, the speed of propagation of explosive transformation nonetheless will be increased at the expense of the increase of speed of energy transfer of the reaction.

Let us consider first the burning and detonation in gasses and then the same processes in condensed systems.

§ 1. Burning of Gases. Limits of Combustibility

The explosive gasses met in technology constitute, as a rule, mixtures, containing one or several combustible gasses and air or oxygen. Burning in such mixtures can be spread not with any relationship of the components, but only in definite limits of composition, called the concentration limits of combustibility. The minimum content of combustible gas, at which burning is still possibly is called the lower limit of combustibility, the maximum content — upper limit. These limits are not absolute constants of the mixture of given gasses, but to a significant measure depend on the conditions.

Since the possibility of burning is caused by the chemical reaction rate and speed of energy transfer to unreacting substance, then all factors, which affect the speed of the reaction and energy transfer, will correspondingly reflect on the possibility of burning.

The direct cause, determining the impossibility of propagation of burning of very diluted and therefore, slowly burning mixtures, is, according to Zel'dovich, the loss of heat by thermal radiation.

The exact knowledge of the limits of combustibility for specific conditions has a large practical value from the point of view of safety engineering. Knowing the limits, it is possible, by strictly limiting the content of combustible gas, to prevent the possibility of formation of dangerous mixtures. Thus, for instance in gas coal mines, the formation of a methane-air mixture, containing more than one percent methane (lower limit of combustibility is 5%) is not allowed. If, however, such a mixture was formed it is prohibited to charge blast holes in the mine and all the more so to detonate them until as the content of methane does not go below 1%.

Besides the mining industry (coal mines, potassium, and other pits, petroleum mining and others), explosive gas mixtures are also met in metallurgic, coke-chemical, oil refining and gas factories and in all chemical productions, where volatile solvents are used.

Let us consider the basic factors affecting the limits of combustibility of gasses.

Certain impurities, which retard the reactions of burning, render a strong influence on the limits of combustibility. The most active halogen derivative hydrocarbons, which with a small content give noncombustible mixtures of carbon oxide, hydrogen or hydrocarbons with air. Thermal properties of mixtures with such additions are changed little and significant deceleration of the reaction plays a basic role and consequently also the speed of propagation of the burning, leading to an increase of thermal loss. Thus, the moist mixture $2CO + O_2$ burns with a speed of 90 cm/sec, after the addition of 1.8% carbon tetrachloride the burning rate decreases to 40 cm/sec; and almost the limit with a content of 4.5% CCl_4 constitutes only ~4 cm/sec.

The addition of inert gasses narrows the limits and finally gives an incombustible mixture. This influence in general is proportional to the heat capacity of the inert addition. Figure 4.1 shows the influence of nitrogen and carbon dioxide on the limits of combustibility of mixtures of hydrogen, carbon oxide and methane with air. As can be seen, carbon dioxide lowers combustibility stronger than nitrogen, added in the same quantities.

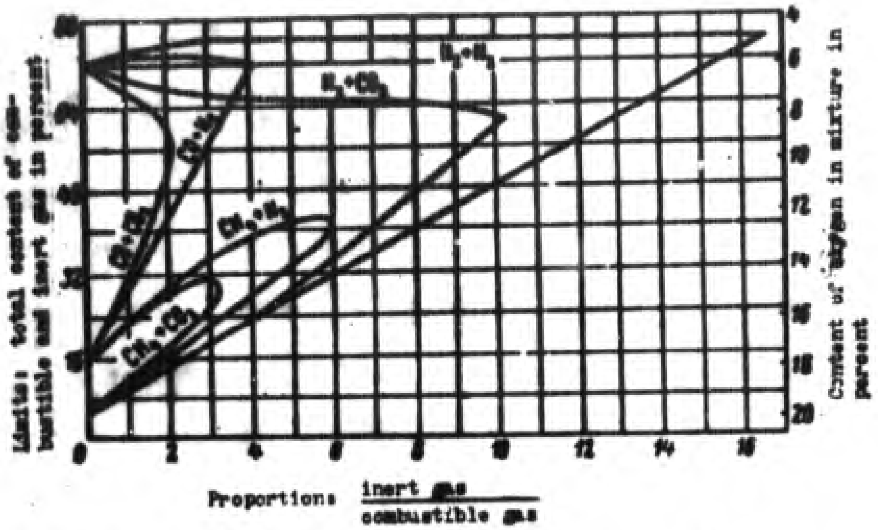

Fig. 4.1. Limits of combustibility of mixtures of hydrogen, carbon oxide and methane with air with the addition of different quantities of nitrogen or carbonate.

An addition, able to react with the absorption of heat, turns out to be more effective with respect to lowering combustibility. Thus, if stoichiometric mixture of methane with air is diluted with nitrogen or methane, then it turns out that it is sufficient to add 5 times less methane than nitrogen, in order to make a mixture incombustible. The effectiveness of methane is explained by the fact that at a high temperature it enters with the products of burning in endothermic reactions (for instance, $CH_4 + CO_2 \rightleftarrows 2CO + 2H_2 - 56$ kcal).

The limits of combustibility depend also on the direction of propagation of the flame. With propagation of the flame from bottom to top, the limits are wider than with propagation in a horizontal direction or from above.

The increase of the diameter of the container, as a rule, expands the limits of combustibility, especially noticeably with small (up to 5 cm) diameters. This influence, apparently, should be connected with the cooling action of the walls, which becomes relatively less with an increase of the diameter of the container.

The safety lamp device of Davy is based on the cooling action of small diameter holes. Mesh in the metallic protective screen of this lamp is so small that a flame cannot penetrate through it. On the same principle the design of explosion proof electric equipment is based. The apparatus consists of a durable metallic housing with flanges; gaps among these flanges must be so small that a flame, if it appears in the apparatus, cannot penetrate its limits.

The limits of combustibility do not depend on the length of the tube with its ends open, an increase of length in closed tubes narrows the limits.

Atmospheric humidity, entering in the composition of the mixture, renders a weak influence on the limits of combustibility. The upper limit for the methane-air mixture in the presence of water is somewhat lowered, since water vapor replaces part of the oxygen necessary for combustion of the methane; for a dry mixture the limit constitutes 14.02% and for a wet, 13.54%. Carbon oxide occupies a special position. For that gas the influence of humidity is more significant. During propagation of the flame from the bottom to the top in a tube with a diameter of 5 cm, the lower limit constituted for a saturated water mixture 13.1% for a day, 15.9%.

The change of pressure within the limits of normal oscillations of atmospheric pressure does not affect limits of combustibility. With large changes of pressure the limits of combustibility are changed, although not equally for different mixtures. In general the decrease of sub-atmospheric pressure narrows the limits, therefore, with certain sufficiently low pressure the upper and lower limits coincide; with smaller pressure, the mixture of any composition is not capable of propagation of a flame. This dependence is schematically shown in Fig. 4.2 for a mixture of carbon oxide with oxygen.

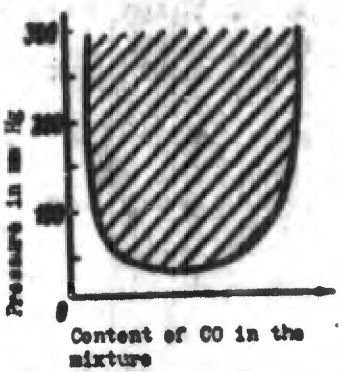

Fig. 4.2. The influence of pressure on the concentration limits of combustibility of a mixture of carbon oxide with oxygen. The region of combustibility is shaded.

An increase of pressure higher than 1 atm (tech.) often, although not always, expands the interval of combustibility (Fig. 4.3). For certain mixtures, for instance hydgoren with air the limits of combustibility with an increase of pressure from 1 to 125 atm (tech.) does not depend on the pressure.

For a mixture of CO with air with an increase of pressure the limits are narrowed somewhat. Narrowing of limits with an increase of pressure is explained by a decrease of the content of water vapor, which renders a strong influence on the burning rate of the given mixture.

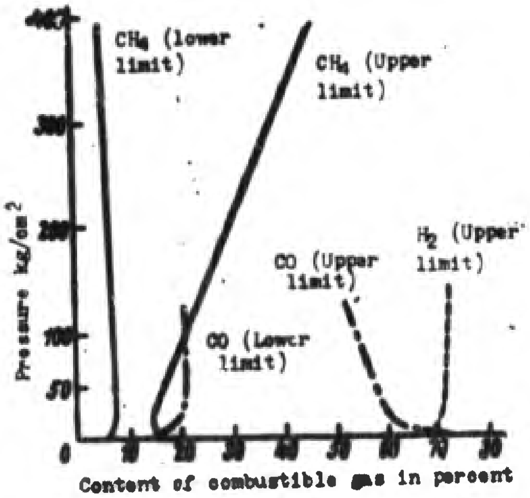

Fig. 4.3. Limits of combustibility of mixtures of hydrogen carbon oxide and methane with air at pressures higher than atmospheric.

For the methane-air mixtures, the lower limit practically does not depend on the pressure during a change of pressure from 1 to 400 atm (tech.), then as the upper limit sharply increases (from 15 to 46%). This influence of pressure on the upper limit of the methane-air mixture is explained by the fact that at high pressures methane becomes thermodynamically stable and does not enter in endothermic reactions flowing with the increase of the number of molecules. Therefore, with an increase of pressure the sluggish influence of the surplus of methane is weakened. Besides this the high perssure increases the speed of the reaction, positively influencing, thus, its ability to self-propagation.

An increase of temperature expands, as should be expected, the limits of combustibility. In the coordinates "percentage of combustible gas-temperature" this expansion is expressed by straight lines (Fig. 4.4). According to White at 20°C the mixture of hydrogen with air can burn with a content of H_2 from 9 to 72%, at 400°C the limits of combustibility constitute accordingly 6.3 and 82%.

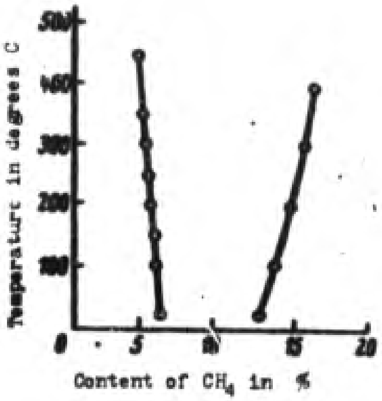

Fig. 4.4. Influence of initial temperature on limits of combustibility of mixture of methane with air.

Mixing somewhat expands limits, as was established during experiments with a mixture of ether with air, and lowers the lower limit of methane and ethane-air mixtures.

The lower limit of the mixture with oxygen for the majority of gasses is the same, as the mixture with air. The upper limit for an oxygen mixture always is significantly larger than for air.

During experimental determination of the limits of combustibility, it is necessary to consider the change of inflammability of the mixture depending on its composition. A quantitative characteristic of inflammability is the minimum magnitude of energy of the igniting impulse, sufficient for excitation of burning. For a mixture of a given combustible gas with air other things being equal, there is a certain optimum composition, at which its inflammability is the greatest. With deflection from this composition in the direction of

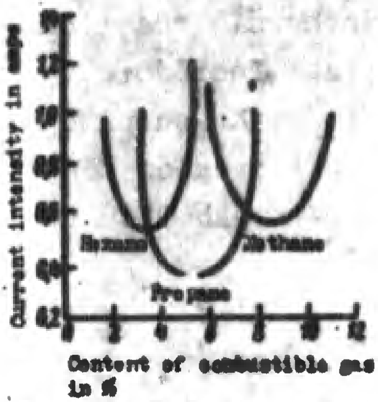

Fig. 4.5. Dependence of minimum capacity of igniting spark (current intensity in primary chain) on composition for mixtures of methane, propane and hexane with air.

smaller or larger content of fuel, inflammability decreases. This relationship is illustrated in Fig. 4.5, which gives the dependence of the minimum capacity of igniting spark on the composition for mixtures of methane, propane and hexane with air. Therefore, if for determination of limits igniting impulses of different intensity are used, then with weak impulses the interval between the limits of combustibility will appear rather than with strong impulses.

It is obvious, however, that for a mixture of given gasses there are absolute limits of combustibility, not dependent on the intensity of initiation. For these limits a flame loses the ability to self-propagation at any intensity of initial impulse. For methane with air, for instance, these limits constitute 5 and 14%.

For a mixture, containing several combustible gases, the limit of combustibility can be calculated by the formula of Le Chatelier, founded on the assumption concerning the additive ability of the combustibility of gases;

$$\frac{n_1}{N_1}+\frac{n_2}{N_2}+\ldots+\frac{n_k}{N_k}=1,$$

where $N_1, N_2, \ldots, N_k$ – limits of combustibility (in %) for every individual;

$n_1, n_2, \ldots, n_k$ – the percentage of every combustible gas in the mixture, corresponding to the limit.

By means of a simple conversion formula it is possible to reduce to the form

$$L=\frac{100}{\frac{n_1}{N_1}+\frac{n_2}{N_2}+\ldots+\frac{n_k}{N_k}}, \qquad (4.1)$$

where m_1, m_2... – is the percentage of each combustible in the initial mixtrue of combustible gasses, $\Sigma m = 100$;

L – is the total percentage of combustible gasses in mixture of them with air, corresponding to the limit.

In many cases (for instance, for mixtures of hydrogen, carbon oxide and methane) the formula is executed exactly enough (better for the lower limit, worse for the upper); in other cases, especially when one of the components is a vapor, significant deflections are observed.

As an example of the use of the formula of Le Chatelier the lower limit for natural gas of the following composition will be calculated (in %):

methane......................	80	(lower limit 5.3%)
ethane.......................	15	(lower limit 3.22%)
propane......................	4	(lower limit 2.37%)
butane.......................	1	(lower limit 1.86%)

$$L = \frac{100}{\frac{80}{5.3} + \frac{15}{3.22} + \frac{4}{2.37} + \frac{1}{1.86}} = 4.55\%.$$

Data on the limits of combustibility of gasses and vapors are given in Appendices 1 and 2.

§ 2. Speed of the Burning of Gases. Transition of Burning into Detonation

1. Methods of Determination of the Burning Rate

The burning rate ("normal" burning rate) is called the speed of frontal shift of the reaction of relatively unburned gas, counted off in the direction of the normal to the surface of the front.

For determination of the burning rate of gasses Bunsen used the following method: a gas mixture is released through a narrow hole of the burner and the maximum escape velocity of the gas, at which the flame was held exactly at the hole, but still did not skip inside was determined. It is obvious that this speed of gas is equal to the burning rate. For detonating gas Bunsen found a burning rate equal to 34 m/sec for a mixture of carbon oxide with oxygen 1 m/sec.

V. A. Michalson used an original method of determination of the burning rate. He photographed the cone of the flame, forming during burning. The product of the area of the lateral surface of the cone at the burning rate is equal to the volume of gas, flowing per unit of time, hence it is easy to calculate the burning rate.

Subsequently for determination of the burning rate photographic methods have obtained wide use. In case of sufficient actinism of flame, for instance, for mixtures of carbon oxide or hydrocarbons with air, it is possible to photograph directly, otherwise, for instance, for the flame of hydrogen a change of optical density in the burning front can be used during the transition from unburned gas to products of combustion, which can be photographed by special methods.

During propagation of burning of a gas mixture in a tube or in a spherical container usually the shift of the flame front is photographed on photographic film, secured on a revolving drum, the axis of which is parallel to the direction of propagation of burning (Fig. 4.6). Knowing linear speed of film, it is possible by the slope of the image of the flame obtained to calculate the speed of its propagation in the tube.

It is necessary to consider that the speed of propagation of the flame of a relatively motionless container, determined by these methods, as a rule, is not equal to the normal burning rate, since in usual conditions of the experiment (burning in a closed container) unburned

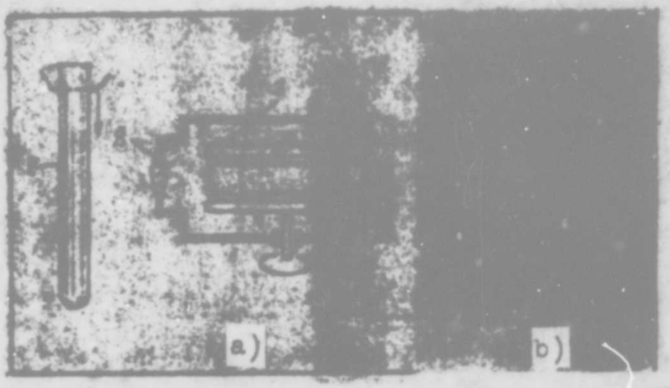

Fig. 4.6. System of photographic determination of the speed of propagation of a flame (a) and samples of photographs of burning (b). 1 — drum; 2 — lens; 3 — tube with gas.

gas also goes into motion due to the growth of pressure. In this case the speed of propagation of the flame is equal to the sum of the burning rate (propagation of flame is a relatively unburned gas) and the speed of the gas. Furthermore, the surface of the front of the flame usually is not flat and can change its form in the course of burning. Therefore, during a calculation of the normal burning rate according to the values of the speed of propagation of flame obtained by photographic methods, it is necessary also to consider the form of the front of the flame, which determines the surface of burning, and the speed of the unburned part of gas, if it is not equal to zero. The form of the front of the flame one can be determined by instantaneous photographs of the flame on motionless film.

Knowing the diameter of the tube d and the speed u_p of the propagation of the flame, it is possible to calculate the volume of gas v, burning per unit of time,

$$v = \frac{\pi d^2}{4} u_p.$$

[p = p = propagation]

In turn this volume obviously is equal to the product of the surface of the front of the flame at a normal burning rate u_n. Having this data, it is possible to calculate the normal burning rate.

As example in Table 4.1 are given the results of calculations of the normal burning rate of the methane-air mixture (10:90) in tubes of different diameters. During significant oscillations of speed of the propagation of the flame, the value of the normal burning rate is obtained practically constant.

Table 4.1. Speed of Propagation of Flame of Methane with air in Tubes of Different Diameters and the Norm Speed of Burning Calculated from this Data

Diameter of tube in cm	Observed speed of propagation of flame in cm/sec	Area of the front in cm^2	Normal burning rate cm/sec
10	110	300	29
10	71	190	29
5	92	66	27
5	61,5	48,5	25
2,5	71,5	12,6	28
2,5	63	11,0	28
2,5	59	10,4	28

2. Factors Affecting the Burning Rate

The normal burning rate depends on the composition of the mixture, pressure, initial temperature and the presence of impurities.

If one were to change the composition of a mixture, then with a certain content of combustible gas, usually larger than that, which corresponds to complete combustion, the speed of burning passes through the maximum. By measure of approximation to the limits, the speed drops, but in the limits is not equal to zero, but has certain finite values. Figure 4.7 represents the dependence of the normal (on the left) and mass (on the right) burning rates of a mixture of hydrogen and air on the composition.

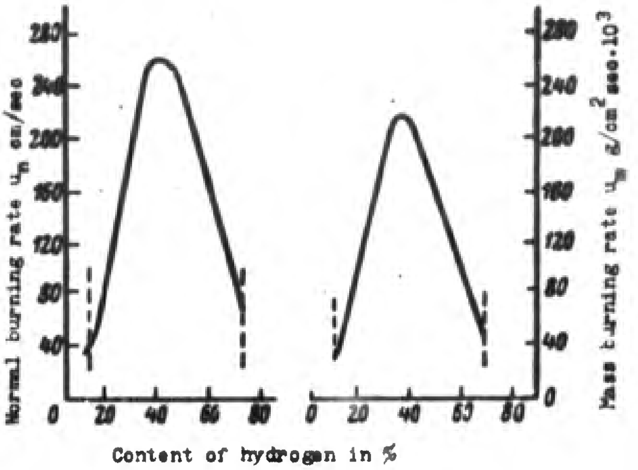

Fig. 4.7. Dependence of normal (on the left) and mass (on the right) burning rates of a hydrogen-air mixture on the composition.

Table 4.2 gives the magnitude of the maximum burning rate for mixtures of a number of gasses with air.

An increase of pressure can in different ways affect the burning rate of different mixtures. Frequently a lowering of speed is observed. Thus, for instance, with increase of pressure from 1 to 4 atm (tech.) the normal burning rate of a methane-air mixture drops twice; in the case of a mixture of carbon oxide with air the speed also drops (0.42 and 0.24 m/sec, correspondingly). In the second case the maximum of the normal burning rate at a pressure near 300 mm of mercury column is observed.

Table 4.2. Maximum Burning Rate of Different Combustible Gasses in a Mixture with Air

Combustible gas	Burning rate $u_{n\,max}$ in cm/sec	Content of combustible gas in % by volume	
		in a mixture having the maximum burning rate	in a stoichiometrical mixture
Hydrogen	267	42	29,5
Acetylene	131	10	7,7
Ethylene	63	7,0	6,5
Carbon bisulfide	48,5	8,2	6,5
Propylene	43,5	4,8	4,5
Carbon oxide +1.2% H_2O	41,5	53	29,5
Benzene +0.5% H_2	38,5	3,0	2,7
Ethyl ether	37,5	4,5	3,4
Methane	37,0	10,5	9,5
Cyclohexane	35,0	2,5	2,3
n. Pentane	35,0	2,9	2,6
n. Hexane	32,9	2,5	2,2
Acetone	31,8	6,0	5,0

In fuel-air mixtures, the burning rate decreases with an increase of pressure, but less than the density increases, in other words, the mass burning rate is increased.

Oxygen mixtures give some dependence of the burning rate on the pressure than to air. Their normal burning rate does not depend on pressure, as is shown for a mixture of carbon oxide with oxygen in Fig. 4.8. Correspondingly, the mass speed increases proportionally to the pressure.

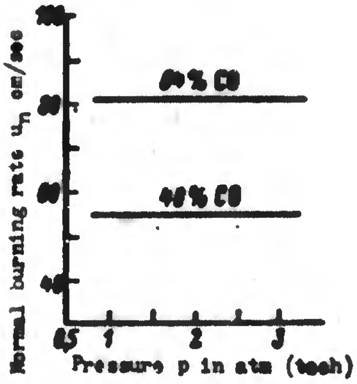

Fig. 4.8. Normal burning rate of mixtures carbon oxide with oxygen at different pressures.

An increase of temperature increases the burning rate, although relatively weakly. Thus, with an increase of the temperature of the mixture of carbon oxide with air from 20 to 460°C the normal burning rate increases from 0.42 to 0.85 m/sec. For a methane-air mixture during the transition from 20 to 430°C. The normal burning rate is increased from 0.31 to 0.64 m/sec.

Inert impurities decrease the burning rate. As an example Fig. 4.9 shows the influence of an impurity of nitrogen on the normal burning rate of mixtures of carbon with oxygen.

Active impurities, which affect the speed of chemical transformation not only as a result of dilution of reagents, sometimes even with a small content strongly change the burning rate. Figure 4.10 gives the dependence of the normal burning rate u_n of a mixture of carbon oxide with oxygen on the content of water. In the presence of water the reaction flows by another, faster, way than without it. The thorougly dried mixture, in general, cannot be ignited. A very small content of water vapors transmits the ability of burning to the mixture. An increase of the content of water up 9% (at atmospheric pressure) leads to an increase of the burning rate. With a still larger content of water the burning rate drops, since the diluting action of water starts to predominate. Burning of the given mixture is accelerated not only by water, but also by other water containing gasses (for instance, hexane), although by themselves these gasses in mixtures with oxygen burn slower than a slightly wet mixture of carbon oxide.

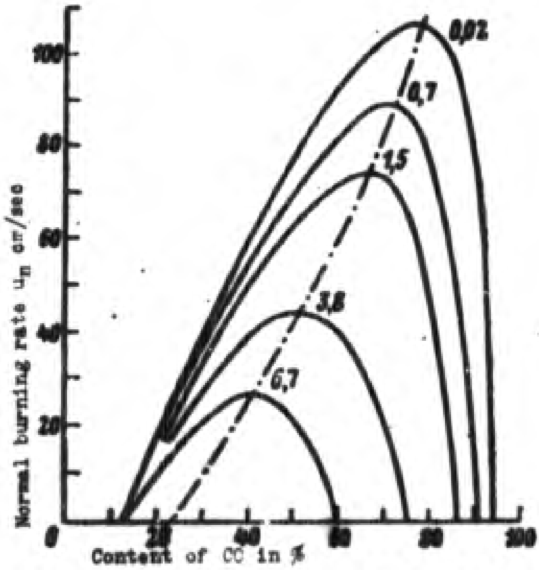

Fig. 4.9. Influence of the addition of nitrogen of normal burning rate of mixtures of carbon oxide and oxygen. The curve numbers signify the relation of the content of nitrogen and oxygen in the mixture (by volume).

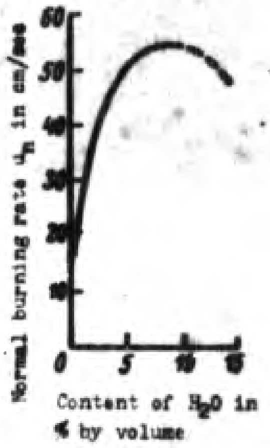

Fig. 4.10. Dependence of the burning rate of a mixture of carbon oxide with oxygen on the content with water.

3. Transition of Burning to Detonation

There is slow uniform propagation of stable burning only when it is not accompanied by an increase of pressure, for instance, if burning occurs in a tube open at one end with ignition at this end. When burning occurs in a closed space or the exit of gasses is hampered, products of the reaction are not only heated adjacent to the front of flame layer of the unburned gas by means of thermal conduction, but also, being expanded at the expense of high temperature, the unburned gas is led into motion. Braking of a layer of gas, adjacent to walls, leads to irregularity of speed by section of tube; the flame is extruded in the direction of propagation, as a result of which the surface of the front of burning is increased and the quantity of gas burning per unit of time. Along with this the surface of the front (in the case of a horizontal tube during burning from bottom to top) increases also due to convection, and with corresponding aerodynamic conditions and consequently the turbulence of the unburned gas. A typical form of the front of a flame is shown in Fig. 4.11.

Fig. 4.11. Instantaneous photograph of the front of the flame during burning of a gas mixture in a horizontal tube.

Acceleration of the propagation of the flame due to the enumerated causes strengthens the compression of the unburned gas before the front of the flame. This compression spreads the unburned gas in the form of consecutive weak shock waves. Every subsequent wave increases in speed, greater than the preceding and correspondingly overtakes it. In a certain distance before the front of the flame the totality of shock waves is joined in one powerful shock wave. The appearance of such a wave leads to strong compression and heating up of the gas.

When the temperature in the shock wave becomes sufficiently high, new stable conditions of propagation of the reaction appear — detonation, at which the transmission from layer to layer of energy provoking chemical reaction is carried out not by means of a slow process of thermal conduction, but by means of propagation of a shock wave. The speed of detonation is measured by thousand meters per second, when the normal burning rate not exceed 10-15 m/sec, usually occurring significantly less.

The described mechanism of the transition of burning of gasses to detonation explains why the appearance of a detonational wave occurs at a certain distance before the front of the flame, before the flame approaches this point. Schematically this process is shown in Fig. 4.12.

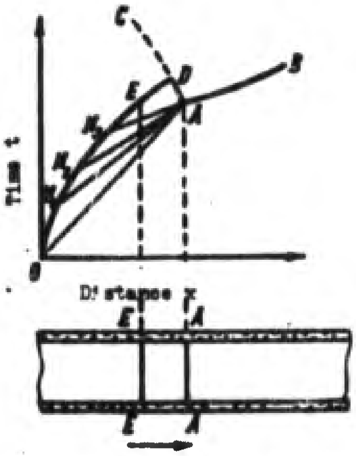

Fig. 4.12. Diagram of propagation of shock waves during accelerated burning and appearance of detonation.

The way of the accelerated flame in the coordinates "time — distance along the axis of a tube" is represented by the OD curve. Consecutively the outgoing shock waves are shown by the lines OA, N_1A, N_2A etc. Detonation appears at point A when the front of the flame is at point E; to the right of point A the detonational wave AB spreads, to the left — also the detonational wave AD, transformed after an encounter with the front of the flame in the shock wave DC (the so-called detonator), spreading by the products of burning.

A photograph of the process of transition of burning of a gas mixture to detonation is shown in Fig. 4.13.

Fig. 4.13. Appearance of detonation during burning of a gas mixture (flame spreads to the right from above).

One of the characteristics of the inclination of burning of a gas mixture to transition to detonation is the magnitude of the <u>predetonational section</u> — the distance from the place of ignition to the place of the appearance of detonation. This distance depends on a number of factors. Thus, with an increase of initial pressure the predetonational section is reduced. For a mixture of $2H_2+O_2$ with an increase of pressure from 1 to 6.5 atm (tech.) the length of a predetonational section is decreased from 70 to 27 cm. With an increase of the length of tube the predetonational section increases. There is, however, a certain minimum length of tube with the decrease of which detonation does not appear.

With an increase of the diameter of the tube the appearance of detonation is hampered. This influences the increase of initial temperature. During an explanation of this phenomenon it should be considered that an increase of temperature at constant pressure signifies a decrease of the density of gas, i.e., a decrease of the concentrations of reagents.

Roughness of walls of the tube strongly reduces the predetonational section and expands the concentration limits of the transition of burning to detonation. There are mixtures (for instance, benzene + + air), which burn without transition to detonation in tubes with smooth walls and detonate in tubes with rough walls.

Dilution of the mixture by inert gasses or a great surplus of one of the components increases the predetonational section. For mixtures of acetylene with oxygen, nitrogen oxide and nitrous oxide the dependence of the magnitude of the predetonational section on the composition (according to Le Chatelier) is given in Table 4.3.

There are known critical values of the composition and pressures, which limit the region, outside of which spontaneous transition of burning to detonation is impossible. The interval between these is a concentration limits rather than an interval ov combustibility. For certain mixtures the value of the given limits (which are sometimes called "explosive limits") are given in Table 4.4.

Table 4.3. Dependence of the Magnitude of the Predetonational Section on the Composition of the Gas Mixture

Composition of mixture	$C_2H_2 + 1\frac{1}{2}O_2$	$C_2H_2 + O_2$	$C_2H_2 + 8O_2$	$C_2H_2 + 10O_2$	$C_2H_2 + 2NO$	$C_2H_2 + 6NO$	$C_2H_2 + 2N_2O$	$C_2H_2 + 6N_2O$
Predetonational section in cm	100	5	15	80	20	50	100	10

Table 4.4. Concentration Limits of the Ability of Certain Mixtures to the Transition of Burning to Detonation at Atmospheric Pressure

Mixture	Content of combustible gas by volume in %	
	Lower limit	Upper limit
H_2 + air	27	35,5
$H_2 + O_2$	23	85
$CO + O_2$	60	78
$CH_4 + O_2$	10	60
C_2H_2 + air	6,6	15,2

On the length of the predetonational section essentially influences the character of the initial impulse has essential influence. From the explosion of the capsule-detonator the detonation of gasses starts practically instantly. During ignition by an electrical spark burning appears, which only after a comparatively large section of acceleration can cross to detonation.

In conclusion let us note that not only the above described transition of burning to detonation is possible, but also the inverse process — the transition of detonation to burning, sometimes leading even to complete damping of explosive transformation. Such phenomena were observed, for instance, during undermining of acetylene in a narrow long tube. In the experiments of lafite the transition of detonation to burning took place during a sudden increase of the diameter of the tube, containing the gas mixture.

§ 3. Detonation of Gases

The detonation of gas mixtures was discovered by Bertlo and William and simultaneously by Mallyar and Le Chatelier in the last quarter of the past century. These authors developed new technology of experiment and investigated the basic characteristics of the phenomenon of detonation.

Let us give briefly the condition and results of the experiments of Bertlo and V'el with a stoichiometrical mixture of hydrogen and oxygen. The experiments were placed in a rubber tube with a diameter of 5 mm, and a length of 40 m. For excitation of detonation an electrodetonator with pressed mercury fulminate was used. For propagation of detonation two lines of tin foil were broke, included in the electrical chain of the chronograph. By the magnitude of the time interval between breaks the average speed of detonation was calculated.

The experiments showed that the speed of detonation (~2810 m/sec) depends neither on the position of the tube (vertical, horizontal or parallel rows) nor on its length. The material of the tube (rubber, glass, lead) also does not affect the speed of detonation. With a change of the diameter of the tube the speed of detonation remains constant under the condition that the diameter does not decrease lower than a certain limit, equal for given mixture to 1-2 mm. In glass tubes with a diameter of 1.5 mm, the speed of detonation decreased to 2341 m/sec. In tubes with closed or open ends the speed of detonation turned out to be identical. The magnitude of the initiating charge of mercury fulminate also did not reflect on the speed of detonation.

Further the researchers developed the dependence of the speed of detonation on the relationship of the components of the gas mixture, on the presence of inert and catalytic impurities, on the pressure and temperature.

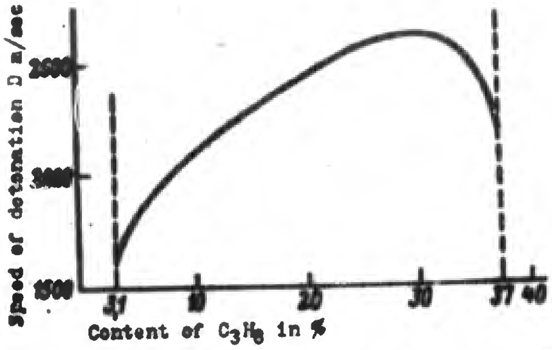

Fig. 4.14. Dependence of the speed of detonation of a mixture of propane with oxygen on the composition.

With a change of the composition of the gas mixture the speed of detonation is changed. For every mixture there is a certain composition which gives the maximum speed of detonation. As example Fig. 4.14 gives a graph of the dependence of speed of detonation D on the composition in the case of a mixture of propane with oxygen. From Fig. 4.14, in particular, it is clear that the ability to detonation is maintained at a definite interval of the composition of the mixture, so that it is possible to talk about the concentration limits of detonational ability similarly, as there was talk above about the limits of combustibility or limits of transition of burning to detonation. The interval of detonational ability is by composition rather than an interval of combustibility, and even more than an interval, in which spontaneous transition of burning to detonation is obtained.

Inert impurities decrease, in general, the speed of detonation of gas mixtures (Table 4.5), inasmuch as they lower the temperature, obtainable during detonation. However, in those casee, when the presence of impurities decreases the average molecular weight of the products of the explosion, this renders a reverse action, which in known conditions can become predominant.

As can be seen from Table 4.5, chemically inert gasses, having

Table 4.5. Influence of Inert Impurities on the Speed of Detonation of Gas Mixtures

Composition of mixture	Speed of detonation in m/sec
$2H_2 + O_2$	2819
$2H_2 + O_2 + 1.5Ar$	1950
$2H_2 + O_2 + 3Ar$	1800
$2H_2 + O_2 + 5Ar$	1700
$2H_2 + O_2 + 1.5He$	3010
$2H_2 + O_2 + 3He$	3130
$2H_2 + O_2 + 5He$	3160
$2H_2 + O_2 + N_2$	2407
$2H_2 + O_2 + 3N_2$	2055
$2H_2 + O_2 + 5N_2$	1822

identical heat capacity — argon and helium — renders with a small content various actions on the speed of detonation of a mixture of hydrogen with oxygen: argon (atomic weight 39) decreases the speed of detonation, and helium (atomic weight 4) — increases. The influence of hydrogen (molecular weight 2) is similar to that of helium. With a very large content of addition its influence predominates in the sense of lowering the temperature, and the speed of detonation decreases in presence of argon, as well as helium. Nitrogen because of a larger than for inert gasses heat capacity and significant molecular weight decreases the speed of detonation of a hydrogen-oxygen mixture both with a large, as well as with a small content.

For several gas mixtures the positive influence of an addition of comparatively small quantities of substances, participating in the reaction of the explosion has been determined.

As an example it is possible to cite a mixture of carbon oxide with oxygen. The presence in this mixture of water vapors or other water containing impurities, for instance, hydrogen sulfide, ammonia, ethylene and so forth, significantly increases the speed of detonation (Table 4.6).

Table 4.6. The Influence of Water Vapors on the Speed of Detonation of a Mixture of Carbon Oxide and Oxygen

Speed of detonation D in m/sec									
mixture, dried over		with a content in the mixture of water vapors of water in % of volume							
P_2O_5	H_2SO_4	1,2	2,3	3,7	5,6	9,5	15,6	24,9	30,4
1264	1305	1676	1708	1713	1738	1693	1666	1526	1266

An increase of pressure somewhat increases the speed of detonation. This influence of pressure, apparently, is combined with a decrease of the dissociation of products of the reaction as a result of an increase of the final pressure during the explosion, as this more specifically will be shown below.

According to Cook with pressures of < 1 atm (tech.) to 50-100 atm (tech.) the speed of detonation of mixtures H_2-O_2-N_2, H_2-O_2-Ar, C_2H_2-O_2 and others, as a rule, increases the pressure by the equation

$$D_{p_1} = D_{p_0} + \beta \lg \frac{p_1}{p_0}. \tag{4.2}$$

On Fig. 4.15 is shown the change of speed of detonation depending on the pressure for mixtures of hydrogen with oxygen in different relationships and also in the presence of argon and nitrogen.

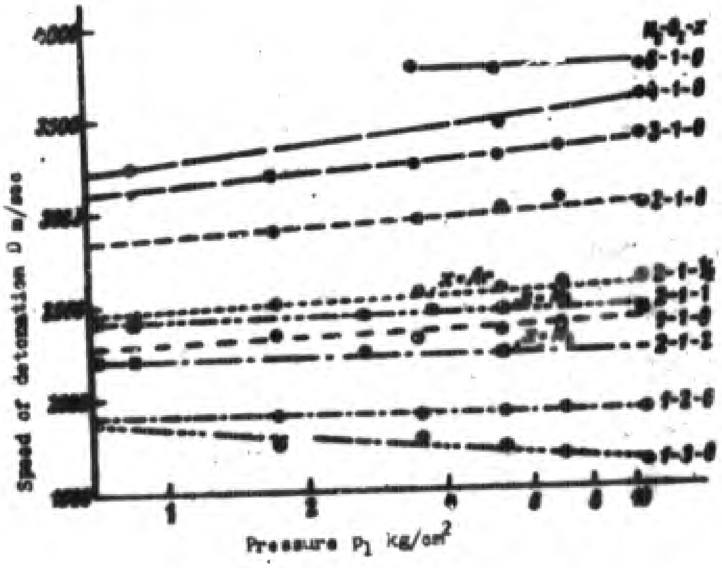

Fig. 4.15. Dependence of the speed of detonation of mixtures of hydrogen with oxygen of different composition on the pressure (density) of the gas.

In Table 4.7 are given the value of constants of the equation (4.2) for certain mixtures.

Table 4.7. Constant of Equation (4.2) for Certain Gas Mixtures

Mixture	p_0 kg/cm²	D_{p_0} m/sec	β m/sec
$6H_2 + 1O_2$	7.0	3600	--
$4H_2 + 1O_2$	7.0	3220	325
$3H_2 + 1O_2$	7.0	3100	250
$2H_2 + 1O_2$	7.0	2850	160
$1H_2 + 1O_2$	7.0	2300	100
$1H_2 + 2O_2$	7.0	1920	10
$1H_2 + 3O_2$	7.0	1890	−240
$2H_2 + 1O_2 + \frac{1}{2}Ar$	7.0	2460	130
$2H_2 + 1O_2 + 1N_2$	7.0	2420	60
$2H_2 + 1O_2 + 2N_2$	7.0	2220	50
$3C_2H_2 + 1O_2$	1,05	2520	0
$2C_2H_2 + 1O_2$	1,05	2600	45
$1C_2H_6 + 1O_2$	1,05	2920	100
$2C_2H_6 + 3O_2$	1,05	2720	150
$1C_2H_6 + 9O_2$	1,05	2200	120

Note: β corresponds to an increase of speed with a tenfold increase of pressure.

The increase of temperature with constant pressure insignificantly decreases the speed of detonation (Table 4.8).

Table 4.8. The Influence of Temperature on the Speed of Detonation of Gas Mixtures

Initial temperature °C	Speed of detonation D in m/sec for a mixture	
	Hydrogen + oxygen	Ethylene + oxygen
10	2821	2581
100	2790	2538

§ 4. Burning and Explosion of Powder-Air Mixtures

Similarly to gas mixtures mixtures of fuels of powder with air or oxygen can ignite and explode. Practically any combustible material suspended in air in finely pulverized form can give an explosion with the igniting of the powder.

Explosions are known in which as powder the following materials participated: carbon, soot, wood, paper, cork, tanbark, bran, chaff, malt, starch, sugar, dextrin, wheat, wool, fiber packing, aluminum, magnesium, tar, sulfur, napthalene, soap and others. According to statistics, in the United States to 1946, (not counting the coal and military industry) 888 dust explosions have occurred in which 575 people died; material damage is estimated at 80 million dollars.

The speed of propagation of a dust explosion is usually less than gas, although the surface of the contact of reagents is less. Although due to this thermal losses are greater, the pressure, obtainable during dust explosions has the same order as during gas, inasmuch as the heat of burning per unit of volume of a dust-air mixture is usually more.

The destroying action of a dust explosion to a significant degree is determined by the obtainable during it of maximum pressure and the speed of its build-up.

The ease of ignition of particles of a dust suspension, and consequently, also its explosiveness depends on number of factors, partially mutually connected: the chemical composition of the dust and gas phase, the form, structure and specific surface of the particles their dimensions, temperature of ignition, energy content necessary for ignition, initial temperature and pressure.

As in the case of gas mixtures, there are <u>lower and upper limits</u>

of combustibility dust-air mixtures by concentration. The exact determination of these limits, especially the upper, is complicated by the difficulty of creating a dust cloud of definite and constant concentration, and also by the dependence of limits on the dimensions of particles, the uniformity of distribution of particles, impurities, intensity and character of igniter and duration of its action.

Thus, with the action of a continuous electrical spark (weak arc), the suspension of finely pulverized coal dust is ignited only with a concentration higher than 35 g/m^3 and during action of a more effective igniter of nitrocellulose, ignition sets in with a concentration, 7 times smaller.

The relative explosiveness of the dust of various materials can be characterized by the minimum quantity of inert dust, which is necessary to add to a combustible, in order to prevent propagation of a flame with certain conditions of ignition. The more intense the igniter, the greater are the necessary additions of inert dust.

Data for certain dusts is given in Table 4.9. In the first column of the table the temperature of a heated tube is shown, through which the dust-air mixture was passed and in subsequent columns — the minimum contents of an inert dust for various powdered fuels.

The chemical composition of the gas phase, especially the content in it of oxygen, strongly affects excitation and propagation of dust explosions. Experience shows that with a decrease of the content of oxygen in a gas phase the temperature of ignition of a dust-air mixture increases. This dependence for finely pulverized coal dust is shown in Fig. 4.16. Figure 4.17 depicts the dependence of the minimum energy, necessary for ignition of a suspension of aluminum by an electrical spark, on the content of oxygen in the gas phase.

Table 4.9. Relative Inflammability of Iron, Magnesium, Zinc and Coal Powder at Different Intensities of Initiation (Temperature of the Tube)

Temperature of tube in °C	Minimum content of inert dust in % for			
	iron, reduced hydrogen	crushed magnesium	zinc powder	coal dust
315	0*			
350	25			
400	43			
500	58			
570	67	0*		
600	70	60	0*	
610	72	60	3	0*
650	77	80	13	45
700	83	90	23	65
750	90	>90	35	80

*The zero values pertain to temperatures of ignition of pure substances, without the addition of an inert dust.

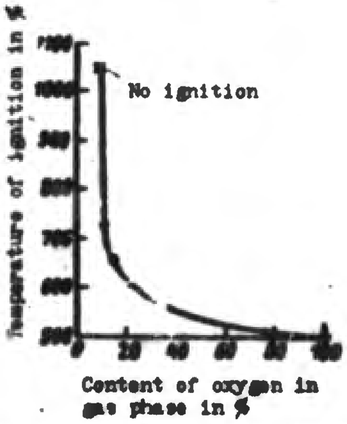

Fig. 4.16. Dependence of the temperature of ignition of finely pulverized coal dust on the content of oxygen in the gas phase.

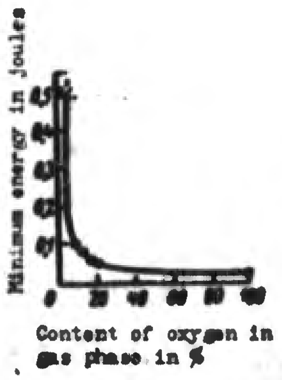

Fig. 4.17. Dependence of the minimum energy of spark, necessary for ignition of an aluminum-air mixture, on the content of oxygen in the gas phase.

<u>The form, structure and surface area of particles of dust</u> play a role, inasmuch as burning occurs on their surface. These factors affect the magnitude of minimum energy, necessary for ignition, on

the pressure of a dust explosion and the speed of its build-up. Table 4.10 gives the value of this energy, pressure and speed of its build-up for three grades of magnesium powder, the first grade consists of particles of approximately spherical form, the second – incorrect angular form and the third – of thin flat particles; mesh composition for all three sorts was approximately identical.

Table 4.10. Minimum Energy of the Spark, Necessary for Ignition of Magnesium Dust-Air Suspensions

Grade of magnesium powder	Energy of spark in joules	Maximum pressure in kg/cm^2	Speed of build-up of pressure in kg/cm^{2}sec	
			Average	Maximum
1st	0,24	4,0	83	102
2nd	0,08	4,4	92	183
3rd	0,08	5,1	102	337

From Table 4.10 it is clear that particles with the most well-developed surface are ignited easiest of all and give great pressure and high speed of its build-up.

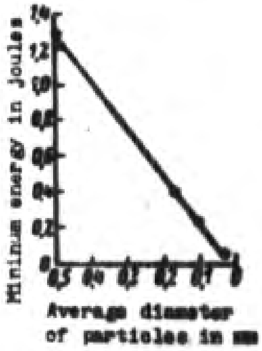

Fig. 4.18. Dependence of minimum energy of a spark necessary for ignition of dust suspension of cellulose acetate in air, on the dimensions of the particles.

Dimensions of particles affect the explosiveness of dust by a number of causes. Small particles are dispersed easier, dispersed, remain in suspension longer and burn faster. Experience has shown that with a decrease of dimensions of particles the energy necessary for ignition decreases (Fig. 4.18), the lower concentration limit is lowered, and the maximum pressure and speed of its build-up increase. With very small particles a further decrease of their dimensions no longer entails an increase of maximum pressure.

The properties of different dusts, characterizing their explosiveness, are given in Table 4.11.

Table 4.11. Characteristic of Explosiveness of Certain Dusts

Substance of dust	Temperature of ignition of dust suspension in °C	Minimum energy of spark necessary for ignition of suspension, in m joules	Lower limit in g/m³	Maximum pressure of explosion in kg/cm²	Speed of build-up of pressure in kg/cm²sec		Limiting content of oxygen, excluding ignition of the dust suspension by electrical sparks in %
					Average	Maximum	
Zirconium	*	15	40	3,5	102	352	**
Magnesium	520	80	20	5,1	309	334	**
Aluminum	645	50	25	6,3	151	401	3
Titanium	480	—	45	3,7	53	116	**
Resin	300	10	15	3,9	88	211	14
Phenol-acetaldehyde resins	500	10	25	4,3	95	221	14
Polyethylene	450	80	25	5,8	28	88	15
Allylalcohol resins	500	20	35	4,8	123	250	—
Cellulose Propionate	460	60	25	4,6	95	165	—
n-Hydroxybenzaldehyde	430	15	20	4,1	151	221	—
Carbon	610	40	35	3,2	25	56	16
Sulfur	190	15	35	2,9	49	137	11
Phenothiazine	540	—	15	3,0	42	102	16
Starch	470	40	45	5,1	74	151	—
Soap	430	60	45	4,2	46	91	—
Aluminum sterate	400	15	15	4,4	53	146	—

*In certain conditions of atomization in air zirconium is ignited at room temperature, apparently, as a result of electric discharge between particles of the dust.

**A decrease of the content of oxygen was attained by an addition of CO_2 to the air. Suspensions of zirconium, magnesium, titanium and certain alloys of magnesium with aluminum ignited in pure carbon dioxide.

The explosiveness of coal dust increases with an increase of the content of volatile substances in the carbon. Coal dusts, containing volatile substances less than 10%, are considered practically nonexplosive.

As shown above, for all combustible dusts inflammability strongly drops with an increase of the content of an inert dust. This action of an inert dust is used by different methods for the fight with propagation of dust and gas explosions in coal mines, in particular, by means of device of screens from inert dust, placed in easily dumping capacities along the way of possible propagation of an explosion. A cloud of an inert dust interrupts the propagation of an explosion. For the same purpose settling coal dust of production (covering of their walls with an inert schistose dust), and also "external" stemming of blast holes from an inert dust are used: the dust is placed before the mouth of the blast hole, and during explosion it is dispersed by the gasses bursting from the blast hole.

The content of combustible gasses in air can increase explosiveness of the dust. Thus, suspensions incapable of explosion with a small content of soot or wood dust became explosive with the addition in the mixture of an illuminating gas in quantities less than the lower limit in the given conditions.

An explosion of a dust-air mixture may be evoked by heating from a flame of an open lamp, a lit match, cigarette, from a broken electric lamp, from friction, from an electrical arc during a short circuit, etc. The ignition by electrical spark is also possible which is formed as a result of spontaneous electrification of dust and the appearance of a discharge during its motion, for instance during pneumatic transportation.

The mechanism of explosion of dust-air mixtures is not fully clarified. It is usually considered that in the case of organic dust the first phase of the process is separation of the dust under the influence of heating up of gasesous combustible substances; in the second phase these gasses in the mixture with air explode; the products of the explosion compress and heat the adjacent layer of dust-air mixture, evoking in it the separation of gasses and dust, etc. Since heating up and gasification of particles of dust requires a certain time, then ignition of a dust-air mixture occurs with a delay similar to that observed, for instance, in the case of the methane-air mixture. In connection with this, during excitation of the explosion of a dust-air mixture an important role is played not only by the high temperature of source being ignited, but also by sufficient duration of its action.

The described mechanism cannot be general at least because dusts not forming volatile combustible substances can explode. The difference between a gas-air and dust-air mixture is only in the degree of dispersiveness of the fuel. In principle the explosion of a dust suspended in air of any combustible substance is possible, independent of its ability to separate during heating of gaseous products. For the possibility of explosion only sufficiently fine crushing of the combustible dust, a definite concentration of it in the air and sufficiently large dimensions of the container (for instance, the diameter of a pipe), in which the dust-air mixture is required.

§ 5. Burning of Condensed Explosive Systems

Burning of condensed systems is used mainly in a weapon for projecting bullets and shells. Therefore, until recently almost exclusively the burning of powders was studied and with this under conditions, close to conditions of practical use (manometric bomb). In such conditions it was often impossible to clarify the dependence of parameters of burning, in particular, its speed on the physical and physicochemical characteristics of the powder.

During the last two decades the study of burning explosives was also studied, which gave an actual picture of this phenomenon, as well as its theoretical interpretation.

These investigations were conducted by a new method — in bombs of constant pressure with burning of a cylindrical charge from face and photographic registration through transparent windows of the character and burning rate, also determination of the average burning rate by the time interval between burnout of two thin wires, intersecting the cylindrical charge at a definite distance from each other was used.

1. Surface Propagation of Burning

Speaking of the burning rate, it is necessary to distinguish two phenomena: <u>itself burning</u>, i.e., propagation of burning inside a solid mass of an explosive by a norm to its surface, and <u>surface propagation of burning</u>, i.e., faster propagation of burning tangent to the surface of the charge, on the boundary of the explosive — the surrounding gas. During burning in air the speed of surface propagation of burning is determined to a significant degree by the reaction of products of burning (if they include combustible gasses) with oxygen of the air. This reaction occurs on the boundary, which touches the explosive, products of burning and air (line AB in Fig. 4.19). Burning of combustible products of incomplete combustion at the expense of atmospheric oxygen leads to an increase of temperature and, as a result, evokes accelerated propagation of burning on the surface of the charge. As a result of this, the face of the ignited from above the cylindrical column of the explosive takes the form of a cone.

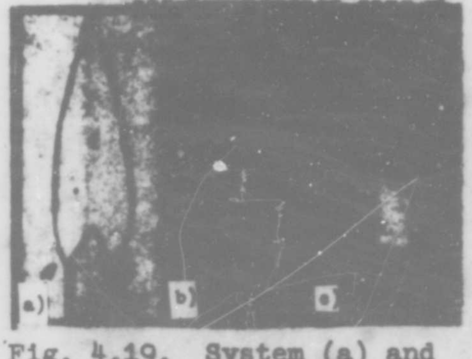

Fig. 4.19. System (a) and photography of cartridge of powder before igniting (b) and during burning in air (c). 1 — products of burning (flame), 2 — powder.

At high speeds of burning, faster propagation of the flame on the surface of the charge is able, according to Belyayev, to occur independent of the reaction with atmospheric oxygen. Due to local increase of pressure in the burning zone not only normal draining of gasses to the surface of the explosive occurs, but also expansion of them along this surface. The gasses contact neighboring particles of the surface of the charge, heat and ignite them.

2. The Limiting Conditions of Burning (Diameter of the Charge, Pressure, Initial Temperature, Density)

Experiments have shown that during ignition from the face of an explosive placed in a cylindrical tube, there will be uniform stable burning only in the case when the diameter of the charge exceeds a certain minimum value. This limit is not an absolute characteristic of an explosive, but depends on the conditions of burning, pressure, initial temperature and others. The higher the pressure and temperature, other things being equal, the less magnitude of the critical diameter. In turn for a given diameter there are limiting values of pressure and temperature, below which burning is dampened.

The critical value of one of the mentioned three parameters with a constant value of the other two and certain conditions of an experiment (material and thickness of the shell) can serve as a comparative characteristic of the ability of the explosive for burning.

As examples it is possible to give the following data. Molten trotyl at room temperature and at atmospheric pressure does not burn in a glass tube with a diameter of 24 mm and burns stably when the daimeter of the tube is increased to 27-28 mm. Tetryl in molten form with the same conditions burns only in tubes with a diameter of more than 6 mm. Nitroglycerine powder with 28% nitroglycerine in the form of solid cylindrical cartridges in a covering from asbestos cord burns at atmospheric pressure and ordinary temperature only when the diameter of the cartridge is not less than 20 mm; at a temperature of

65° a cartridge with a diameter of even 5 mm burns stably. With an increase of pressure to 5 atm (tech.) a cartridge of this diameter burns even at a temperature below zero.

The density* of powdered explosives has a unique influence on the possibility of burning. In the case of a fused explosive like tetryl with a decrease of the dentisy below a certain value burning does not spread. Conversely, for infusible explosives like nitrocellulose a maximum density is observed above which burning stops. The existence of all these mutually connected limits is explained by the following reasons.

Burning occurs as a result of the transmission of heat to a neighboring layer, separating in the reacting layer. Simultaneously with the freeing of heat it is lost through the walls of the tube. Burning becomes stationary only when the quantity of heat, given to the neighboring layer, and thermal loss outside are balanced by incoming heat at the expense of the reaction. If the total heat radiation becomes more than the incoming heat, burning turns out to be impossible.

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*In the technology of explosive substances frequently solid matters in the form of a powder or porous body must be delt with. The density of such a substance, i.e., the mass of the explosive, per unit of volume, occupied by its particles and by the air between them, can be changed within wide limits. The upper of these limits is obviously the density for an explosive which does not contain pores.

The density of a powdered explosive is its important characteristic. For designation of this density science used different terms for explosives: cubic density (corresponding to the German term kubische Dichte), density of charge (corresponding to the French term densite de charge), do not obtain general acknowledgement. Therefore, for brevity we will designate the shown magnitude conditionally simply by the word "density."

In this connection it should be added that the term "gravimetric density" is taken to designate a mass of powdered explosive or powder (in kg) occupying during certain conditions of filling a volume of one liter; the density of loading is called the mass ratio of the explosive or powder to the volume of the container, closed or semiclosed, in which they are enclosed.

With a decrease of diameter of the charge the quantity of heat, separated per unit of time, decreases proportional to the square of the diameter. Heat radiation also decreases, but slower – it is proportional to the surface of the heat withdrawal, i.e., to the first power of the diameter. With a certain value of diameter the heat income cannot compensate for thermal loss and burning is dampened. If with this diameter the pressure is increased, under which the burning goes, then the chemical reaction rate increases, and thermal loss is not changed but burning anew becomes possible. An analogous influence is shown by an increase of the initial temperature.

Damping of burning at both limits of density – lower for fused and upper for infusible powders – has the same cause: an excessive increase of heat withdrawal during burning.

In case of a fused explosive and a small density of powder the gaps between particles are relatively great. The fusion of an explosive, forming on its surface during igniting, under the action of gravity penetrates too deeply in the powder. The liquid comes in contact with a large quantity of solid explosive, which it is in no state to heat to the temperature of intense reaction. Heat radiation from fusion to the depth of the explosive and in the outside exceeds the heat income from the products of burning, the temperature drops and more burning spreads. It is clear that all factors which decrease thermal loss to the outside, for instance, the increase of the diameter of the charge, lower the limiting density.

An increase of the density of an infusible explosive, as for the example of pyroxylin, increases the thermal conduction of the powder. At a certain value of density, heat withdrawal deep into and thermal loss to the outside can become so large that heat income at the expense of the flowing reaction cannot compensate for them, in this case the burning is dampened. The given considerations do not exhaust the condition, at which burning becomes impossible. However, the cause of the impossibility of burning in all cases is the same: excessively great heat withdrawal to the outside and in the depth of the substance, not compensated by heat income at the expense of the reaction.

3. Stationary Burning of Explosives

At those values of the diameter of a charge, pressure and temperature, at which burning is possible, it spreads with a constant speed. This speed does not depend on the diameter of charge, which remains constant during a change of the latter for several times. For nitroglycol this was established with change of diameter from 2 to 24 mm, for trotyl – from 27 to 45 mm. With significantly large diameters (80 mm and higher), for trotyl a certain increase of the burning rate was observed.

The burning rate increases with an increase of pressure and temperature. The dependence of the burning rate on pressure in a definite interval of change of the latter for many explosives studied in this respect can be expressed by the relationship

$$u = A + Bp \quad (4.3)$$

where u = the burning rate;

A, B = constants.

In the case of volatile explosives the value of term A is close to zero, for nonvolatile – this term is of the same order as B.

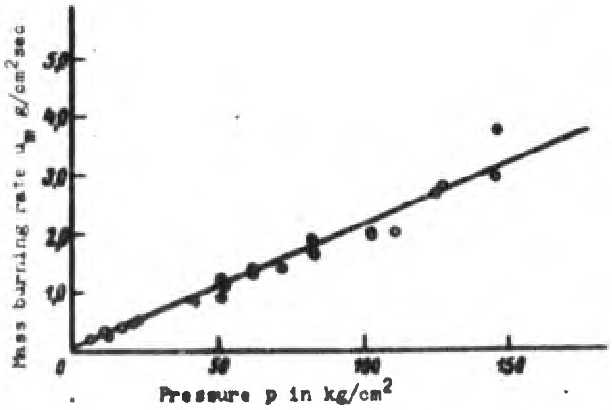

Fig. 4.20. Dependence of burning rate of gelated nitroglycol on the pressure.
[M = m = mass]

Thus, for volatile nitroglycol (in a weak gelatin state), $u_m = 0.075 + 0.0315p$ (Fig. 4.20), for nonvolatile pyroxylin No. 1 $u_m = 0.0907 + 0.0405p$ (in both cases speed is expressed in g/cm^{2}sec, pressure – in kg/cm^2).

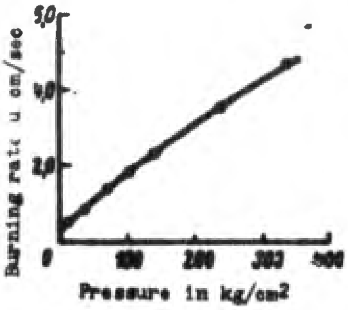

Fig. 4.21. Dependence of burning rate of nitroglycerine powder on pressure.

For nitroglycerine powders in a region of moderate (to ~300 atm (tech.)) pressures of the burning rate as a function of pressure (experimental data shown in Fig. 4.21) may be espressed by the relationships

$$u = A + Bp^{\nu}, \qquad (43a)$$

or

$$u = B'p^{\nu'}, \qquad (4.4)$$

where the constants ν and ν' are less than one.

In the ballistics of a semiclosed volume usually the equation (4.4) is used, inasmuch as it leads to simpler relationships between pressure and parameters of loading.

With large pressures the burning rate of smokeless powders linearly grows with pressure, and in the ballistics of a barrel shot frequently, disregarding term A, the burning rate is taken as directly proportional to the pressure:

$$u = u_1 p, \qquad (4.5)$$

where u_1 is that speed, from which burning of the powder would occur at one atm (tech.), if the shown dependence was executed at all pressures.

Dependence of the burning rate of an explosive on the initial temperature may be expressed by the empirical relationship

$$u = \frac{1}{A_1 - B_1 T_0}, \qquad (4.6)$$

where A_1 and B_1 are constants.

With an increase of the initial temperature by 100° the burning rate of various explosives is increased 1.5-2 times.

The burning rate of nitroglycerine powders at low pressures (1-10 atm (tech.)) depends more on the temperature than at high atm (tech.). The burning rate of black powder and other powders of the mixture type usually is less changed with the temperature than in the case of smokeless powders on the basis of nitroesters.

Burning rate of powdered explosives decreases with an increase of density. With this the mass burning rate usually remains constant. Thus, for pyroxylin No. 1 an increase of density from 0.24 to 0.58 g/cm^3 evokes lowering of the burning rate from 0.61 to 0.26 cm/sec, the mass burning rate constitutes 0.145 and 0.148 g/cm^{2}sec correspondingly.

§ 6. The Theory of Stationary Burning of Explosive Substances

1. Burning of Gases and Volatile Explosive Substances

Construction of the theory of burning of condensed explosives in general, when exothermic reactions occur both in the condensed phase and in the forming gasses, presents a very complicated and up to now unsolvable problem.

The theory of burning of gasses was created by Ya. B. Zel'dovich and D. A. Frank-Kamenetski in 1938. At the same time Belyayev showed that this theory is also used for burning of volatile condensed explosives.

Belyayev noted that many explosives are also volatile at moderate temperatures, when the speed of the reaction in the explosive is still small, the speed of evaporation may be significant. As a result of this during rapid heating of the next layer of the explosive in the process of burning at first evaporation of the explosive occurs, and chemical reactions flow entirely in vapors. For conditions, in which this assertion is just (a small external pressure, highly volatilite explosive in combination with a small constant of speed of reaction in condensed phase), the burning of the explosive can be considered simply as the burning of gas (vapor) with the only difference being that this gas will be formed in the process of the actual burning by means of evaporation of the condensed phase.

Let us consider stationary burning of a volatile explosive in a tube of a constant section. The leading stage of the processes in this case is the propagation of an exothermic chemical reaction in vapors. The heat transmitted from the zone of the reaction to the surface of the explosive forces it to be evaporated with a speed, determined by speed of heat escape. In the condensed phase, chemical reactions do not occur, and there is room only for heating the substance from its initial temperature to the boiling point.

The distribution of temperature in space is shown in Fig. 4.22. T_0 – initial temperature of the explosive, T_b – boiling point, T_{bu} – maximum temperature obtainable during burning. Burning spreads from the left to the right. The surface of the explosive in the considered moment of time is in plane AA. Plane AA, separating the condensed explosive from its vapors (and inasmuch as we are considering the stationary process, also all remaining zones), shifts with speed u from the left to the right.

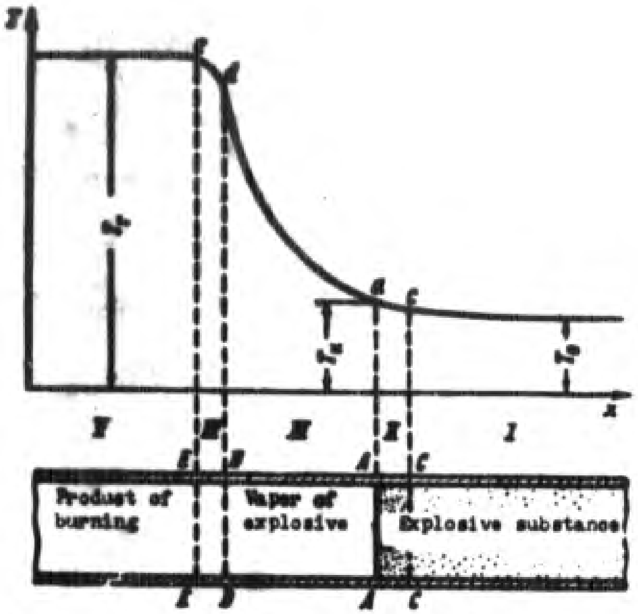

Fig. 4.22. Diagram of the distribution of temperature and flow of the reaction during burning of a volatile explosive according to Belyayev. I — initial explosive; II — heated layer of condensed explosive; III — zone of heating of vapors of the explosive; IV — zone of chemical reaction in vapors; V — zone of products of burning.
[r = bu = burning, к = b = boiling.

Let us consider the process in a system of coordinates, moving together with the front of the burning. In such a system plane AA is motionless and the explosive substance will flow into it from the right to the left with speed u, equal to the burning rate. Being turned into vapors, the explosive will flow with a speed, into so many times larger, so much greater density of vapors less than the density of the condensed substance. By measure of heating up of vapors at the expense of transmission of heat from neighboring layers and liberation of heat during the chemical reaction flowing in them, the speed will grow and after completion of the reaction will attain its maximum value. With this since the process is stationary, the mass speed ($u\rho$), i.e., the mass of the substance flowing through every zone per unit of time, is the same.

To plane AA adjoins a heated layer of the explosive substance AACC. By its thickness it is mathematically convenient to consider the AC section, on which heating up of the explosive decreases in e times.

$$\left(\frac{T_A-T_0}{T_C-T_0}=e\right).$$

Vapors, flowing from the right to the left, are heated at the expense of the heat entering by means of thermal conduction from the zone of high temperature, and also at the expense of liberation of heat by the chemical reaction. With this to the point of inflection of the curve $T = f(x)$ the gradient of temperature grows (by absolute value), at the point of the bend the gradient passes through a maximum and then drops, attaining zero where $T = T_{bu}$. Correspondingly the balance of the flow of heat is also changed; on the right from the point of inflection the element of volume obtains more heat from hot layers than given to it by the cold; on the left from point d, the element of volume of moving gasses issues heat to cold layers more than it obtains from hot. This, of course, does not mean that the reserve of heat and temperature of the element of volume in this zone drop, conversely, they grow due to the increase of temperature which sharply increases the speed of liberation of heat by the chemical reaction.

The equation of heat balance for the element of volume of the reacting gas (vapor), located at a certain distance from plane, AA can be written in the form

$$c_p\rho\frac{\partial T}{\partial t}=-uc_p\rho\frac{\partial T}{\partial x}+\eta\frac{\partial^2 T}{\partial x^2}+F, \tag{4.7}$$

where c_p, ρ, η — the corresponding heat capacity at constant pressure density and thermal conduction of gas, which is assumed does not depend on the temperature,

F — the quantity of heat, separated by the reaction per unit of volume per unit of time (volume velocity of heat emission).

This equation shows that change of thermal energy of the element of volume occurs by three causes:

1) as a result of movement of gas with speed u; 2) at the expense of pure thermal conduction; 3) at the expense of liberation of heat during the flow of the chemical reaction.

Since a live mixture always proceeds from the colder part of the volume, then the first component of the right side of equation is always negative and decreases the quantity of heat at a given point.

The second term, equal to $\eta\frac{\partial^2 T}{\partial x^2}$, is the change of thermal energy of the element of volume at the expense of thermal conduction and can be greater or less than zero. At low temperatures (Fig. 4.22, section cd – the convexity is turned downwards) it is positive, and at high temperatures (section de – convexity of the curve is turned upwards) it is negative.

The third term expresses heat emission at the expense of the proceeding reaction, the speed of which depends on the concentrations of reagents and on the temperature.

Inasmuch as there is talk about the stationary process and it is considered that the zone of burning is motionless, then the distribution of temperature, depicted in Fig. 4.22, does not change in time and in the expression (4.7) it is possible to consider $\partial T/\partial t = 0$ and to replace partial derivatives with full. Then this equation takes the form

$$uc_p\rho\frac{dT}{dx}+\eta\frac{d^2T}{dx^2}+F=0. \qquad (4.8)$$

If it is considered that the zone, where the temperature and chemical reaction rates, and consequently, also heat emission are so small that heat emission can be disregarded, then considering F as equal to zero, the expression (4.7) can be written in the form

$$c_p \rho u \frac{dT}{dx} + \eta \frac{d^2T}{dx^2} = 0. \qquad (4.9)$$

Introducing the variable $\varphi = \frac{dT}{dx}$, will obtain

$$c_p \rho u \varphi + \eta \frac{d\varphi}{dx} = 0$$

or

$$\frac{d\varphi}{\varphi} = -\frac{c_p \rho u}{\eta} dx,$$

whence after integration we find

$$\ln \varphi = -\frac{c_p \rho u x}{\eta} + C_1.$$

Since

$$\frac{c_p \rho}{\eta} = \frac{1}{\varkappa},$$

where $\varkappa$ is the temperature transfer, when

$$\frac{dT}{dx} = e^{C_1} e^{-ux/\varkappa}. \qquad (4.10)$$

whence

$$T = e^{C_1} \frac{\varkappa}{u} e^{-ux/\varkappa} + C_2 \qquad (4.11)$$

The integration constants C_1 and C_2 we determine from the condition that with $x = \infty$

$$T = T_0,$$

and with $x = 0$

$$T = T_k;$$

Then $C_2 = T_0$ and

$$e^{C_1} = \frac{u}{\varkappa}(T_k - T_0).$$

Placing these constant in the expression (4.11) we obtain the dependence of temperature T on the distance x, measured from the plane with temperature T_b, in the form

$$T=T_0+(T_s-T_0)e^{-\frac{u}{\varkappa}x}. \qquad (4.12)$$

This relationship in reference to burning was conducted for the first time by Michaelson; it is accurate for a zone, in which heat emission of the flowing chemical reaction can be disregarded.

In that region of temperatures, where heat emission becomes essential at the expense of the reaction, term F in the expression (4.7) is maintained. This equation can be converted by the following form.

The speed of heat emission F depends on the concentration of reactants and on the temperature. Connecting the concentration with temperature, it is possible to express the speed of reaction and speed of heat emission as a function of one temperature. With this an equation of the second order is obtained, nonlinear in the form of a nonlinear dependency F(T).

For the solution of this equation Zel'dovich used that property of the law of Arrhenius that the speed of a reaction strongly depends on the temperature, if, as usual, the condition is executed

$$E\gg RT. \qquad (4.13)$$

The dependence of the speed of heat emission of reactions of zero, first and second orders on the temperature for typical conditions of burning ($T = 300^\circ K$; $T_{bu} = 1900^\circ K$; $E = 50{,}000$ cal/mole, is shown in Fig. 4.23.

When the condition is fulfilled (4.13), it may be assumed that practically the entire reaction flows in a narrow temperature interval 0, i.e., between temperatures $T_{bu} - 0$ and T_{bu}, where

$$\theta\ll(T_r-T_0).$$

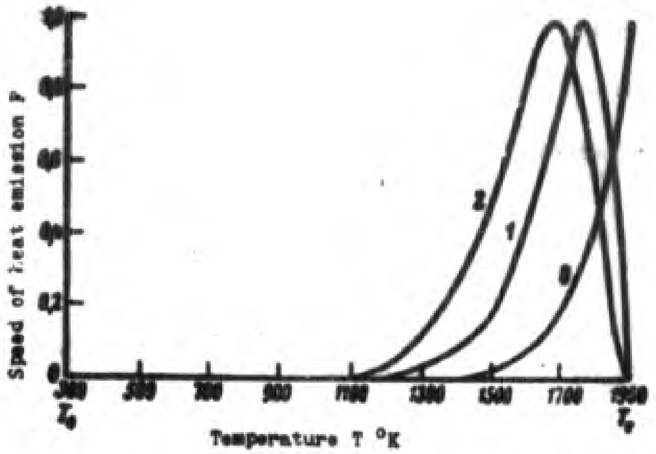

Fig. 4.23. Dependence of volume velocity of heat emission during burning on the temperature. Along the axis of the ordinates speed is placed in conditional units, the maximum value of speed for each of the curves is taken by unit: 0 — reaction of zero order, 1 — reaction of the first order, 2 — reaction of the second order.

Inasmuch as this interval is narrow, then for the zone of the reaction it is possible to disregard the expenditure of heat on heating the reactant, i.e., to assume

$$c_p\rho\frac{dT}{dt}=0.$$

But

$$c_p\rho\frac{dT}{dt}=c_p\rho\frac{\partial T}{\partial t}-uc_p\rho\frac{\partial T}{\partial x}.$$

Inasmuch as $c_p\rho\frac{\partial T}{\partial t}$ also is equal to zero, then $uc_p\rho\frac{\partial T}{\partial x}$ will be equal to zero. Then the equation of heat balance will take the form

$$\lambda\frac{d^2T}{dx^2}+F=0. \qquad (4.14)$$

Equation (4.14) means that in the zone of reaction the elimination of heat by thermal conduction is equal to the heat separated during the chemical reaction.

With the help of equation (4.14) one can determine the magnitude of the flow of heat

$$\eta \frac{dT}{dx}.$$

Again we introduce the variable $\varphi = \frac{dT}{dx}$. It is obvious that

$$\frac{d^2T}{dx^2} = \varphi \frac{d\varphi}{dT}.$$

Supplying this value in equation (4.14), we obtain

$$\eta \frac{\varphi\, d\varphi}{dT} + F = 0,$$

or

$$\eta\varphi\, d\varphi = -F\, dT.$$

Integrating by the zone of reaction, we obtain

$$\eta \frac{\varphi^2}{2} = \int_{T_r}^{T_r - 0} -F\, dT \approx \int_{T_r}^{T_g} -F\, dT = \int_{T_0}^{T_r} F\, dT,$$

whence the gradient of temperature along the boundary of the zone of reaction is approximately equal:

$$\varphi = -\sqrt{\frac{2}{\eta} \int_{T_0}^{T_r} F\, dT},$$

or

$$\eta\varphi = \eta \frac{dT}{dx} = -\sqrt{2\eta \int_{T_0}^{T_r} F\, dT}. \qquad (4.15)$$

In the expression (4.15) the integral of speed of liberation of heat by temperature is undertaken by all regions, in which the speed of the reaction is other than zero. Due to rapid deceleration of the reaction during a drop of temperature the basic component gives a comparatively narrow interval of temperature, adjoining the temperature of burning.

Inasmuch as the expenditure of heat on heating the reacting gas was disregarded, allowing that it is completely eliminated by thermal conduction, then the flow of heat, obviously, can equate the total amount of heat, separating into the zone of burning per unit of time, i.e., the product of the quantity of burning substance in its calorific value Q:

$$-\lambda\frac{dT}{dx}=u_n Q.$$

Putting this expression in the formula (4.15), we obtain:

$$u_n=\sqrt{\frac{2\lambda}{Q^2}\int\limits_{T_0}^{T_r}F\,dT}. \qquad (4.16)$$

Since F = wQ, where w is the volume velocity of the reaction, then

$$u_n=\sqrt{\frac{2\lambda}{Q}\int\limits_{T_0}^{T_r}w\,dT}. \qquad (4.16a)$$

This expression shows that the burning rate increases with an increase of thermal conduction and speed of the reaction at the burning temperature. With this the burning rate is proportional not to the first degree, but to the square root of the speed of the reaction.

The physical meaning of this conclusion is that with an increase of speed of the reaction simultaneously proportional to the growth of burning rate, the thickness of the reacting layer decreases. Thus, if the speed of the reaction is increased m times, and the thickness of the layer will decrease $\sqrt{m}$ times, then the burning rate will also be increased $\sqrt{m}$ times. This can also explain the following considerations.

Quantity of the substance burning per unit of time is equal to $uS\rho$, where S is the area of the section of the charge. On the other hand, if one were to designate the thickness of the reacting layer as h and to consider that the volume velocity of reaction as w and the speed of heat emission as F connected by thc simple relationship $w = F/Q$, then the quantity of the substance reacting per unit of time, obviously, will be equal to $\frac{FSh}{Q}$. Equating both expressions, we obtain

$$uS\rho = \frac{FSh}{Q}. \tag{4.17}$$

whence

$$h = \frac{Qu\rho}{F}.$$

But since from the expression (4.16) $u \backsim \sqrt{F}$,

then

$$h \backsim \frac{\sqrt{F}}{F} = \frac{1}{\sqrt{F}}, \tag{4.18}$$

i.e., the thickness of the reacting layer h is reciprocal to the square root of the speed of the reaction.

Instead of F (4.16) putting its expression through the concentrations of reagents, which are proportional to pressure to the degree corresponding to the order of the reaction, and considering that up to the moment of achieving the maximum temperature, part of the substance has already reacted and is already somewhat diluted by products of the reaction, Zel'dovich obtained the following expression for the mass burning rate:

$$u_m = \sqrt{\frac{2\lambda}{Q}\left(\frac{RT_r^2}{E}\right)^{n+1}(T_r - T_0)^{-n}\, n!\, w_{T_r}}, \tag{4.19}$$

where u_m is the mass burning rate,

E is the activation energy of the reaction of burning,

n is the order of reaction,

$w_{T_{bu}}$ is the speed of the reaction at the temperature of burning.

The formula (4.19) makes it possible to find the dependence of the burning rate on the pressure and initial temperature. In this formula, pressure enters in a latent form, inasmuch as the speed of the reaction $w_{T_{bu}}$ in the gas phase depends on the pressure. Designating by B the product of everything entering in (4.19) magnitudes, which do not depend on the pressure, it is possible to write

$$u_m = Bw_{T_r}^{1/2}.$$

As known, the dependence of the speed of the gas reaction of the nth order on the pressure has the form

$$w_{T_r} = kp^n,$$

where k is the proportionality factor.

Hence

$$u = B_1 p^{n/2}, \qquad (4.20)$$

where $B_1 = Bk^{1/2}$.

Thus, during a monomolecular reaction of burning the speed of it should be proportional to the square root of the pressure; during a bimolecular reaction the burning rate should be proportional to the first degree of the pressure.

The physical meaning of the influence of pressure is that with a large pressure the speed of the reaction above the zone, in which it occurs – the zone of high temperature – moves nearer to the surface of the explosive. Quantities of transmitted heat, and consequently also, evaporated explosive, increase correspondingly to the increase of the chemical reaction rate.

The dependence of the burning rate on the initial temperature of the explosive is determined in the first place by the dependence of the speed of the reaction on the temperature of burning.

$$w_{T_r} \approx A e^{-E/RT_r}.$$

The temperature of burning is $T_{bu} = T_0 + Q/c_p$ (here c_p is the average heat capacity of the products of burning at constant pressure). Thus, the higher the initial temperature, the higher the temperature of burning, the greater the speed of the reaction and correspondingly the burning rate.

In formula (4.19) the temperature of burning in a visible or latent form a number of other factors enter: $Q \sim T_{bu}$, η increases with the temperature, the concentration in the expression for the speed of reaction is a reciprocal temperature. The dependence on the temperature of all factors, entering in expression (4.19) (besides $e^{-E/RT_{bu}}$), can be presented in the form

$$f(T_r) = \gamma T_r,$$

where γ includes all factors, not depending on the temperature.

The total dependence of the speed of burning on the temperature can be expressed by the approximate relationship

$$u = \gamma T_r e^{-E/2RT_r}, \qquad (4.21)$$

or

$$\frac{u}{T_r} = \gamma e^{-E/2RT_r}.$$

By log we obtain

$$\ln\frac{u}{T_r^2} = -E/2RT_r + \ln\gamma. \qquad (4.22)$$

Thus, in the coordinates $\ln\frac{u}{T_r^2} - \frac{1}{T_r}$ the dependence of the burning rate of a volatile explosive on the maximum temperature of burning should be depicted by a straight line, where the tangent of the angle of its slope is equal to E/2R (Fig. 24).

The speed of the reaction in the gas phase, naturally, does not have to depend on the density of the powder, therefore, the mass burning rate does not have to be changed with a change of density. It follows from this that the burning rate should be changed reciprocally to a change of density.

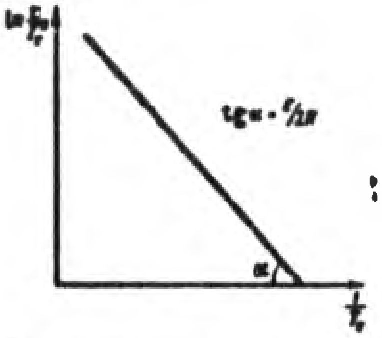

Fig. 24. Dependence of burning rate of volatile explosives on the temperature of burning according to the theory of Belyayev.

Belyayev applied the considered dependences for an analysis of the laws of burning of nitroglycol. He calculated the absolute value of the burning rate, taking that the speed of the reaction is equal to the number of collisions between active molecules, i.e., that the probability factor is P = 1, and obtained very good conformity with the experimental data. In exactly the same way the dependence of the burning rate on the temperature agrees with the experiment. The quantitative conformity of the experiment and the calculation in both cases is obtained, if activation energy is taken as equal to 35,000 cal/mole. The same value of activation energy was obtained also by the temperature dependence of slow disintegration of nitroglycol.

However, subsequent investigations have shown that the given conformity is obtained only in the case when the temperature of burning is considered equal to 1650°K, as calculated by Belyayev on the basis of approximate analysis of the composition of the products of burning. If one were to take the results of exach analysis, then the temperature of burning will appear higher and for achieving conformity of the experiment with the theory it is necessary to take a much larger value of the activation energy than determined for slow thermal disintegration. Calculations of activation energy on the temperature dependence of the burning rate for a number of other nitroesters also leads to values of activation energy, significantly exceeding those determined for slow disintegration.

Besides this, the initial assumption of Belyayev about the fact that the flow of burning and slow homogeneous disintegration is determined by the same reaction, cannot be considered correct. The fact is that at least for nitroesters, the primary stage of thermal disintegration, which determines the speed of its flow, is a separation of the NO_2 group from the molecule of the ester and is weakly exothermic. Such a reaction cannot be conducted during burning which spreads at the expense of the heat separated by the reaction, which provokes heating up of a nearby layer of the substance. During burning there is an exothermic reaction, which separates the main part of the heat and which with the temperature obtainable at the expense of this heat flows with the greatest speed. In the case of nitroesters the leading reaction at low pressures, possibly, is the interaction of nitrogen peroxide with formaldehyde or other aldehydes, which are formed during disintegration of the molecule. A calculation of the burning rate of methylnitrate by kinetic characteristics of the reaction between formaldehyde and nitrogen peroxide leads to satisfactory conformity with the experiment with respect to the numerical value of the speed.

Such conformity between calculation and experiment, however, is not obtained for the temperature dependence on the burning rate. During conclusion of the expression (4.21) we considered only the influence of the initial temperature on the temperature of burning. However, with the initial temperature the explosive is changed essentially and its viscosity, which, as the experiment shows, affects the burning rate. As a result of this, an oversized temperature coefficient of speed is obtained and during calculation by the formula (4.22), not considering the influence of viscosity, can excessively high values of activation energy be obtained.

The assumption about the leading role of the primary monomolecular reaction also contradicts fixed experiments of the proportionality of the burning rate of the first degree of pressure. If a reaction of the first order was leading, then the burning rate by the expression (4.21) would be changed proportional to to the square of the pressure. The change of the burning rate proportionally to the pressure in the first degree agrees with the assumption about the leading role of the reaction between oxygen containing products of primary disintegration like NO_2, on the one hand, and products containing a surplus of hydrogen and carbon, on the other. Such a reaction should go thorugh collisions between the shown particles, and its speed therefore, may be proportional to the product of partial pressure of the reagents, i.e., the square of the total pressure. Accordingly the speed of burning is $u \sim w_r^{1/2} \sim p$.

Thus, the ideal of Belyayev about the mechanism of the burning of volatile explosives can be coordinated with actual laws. Numerical calculations of speed, indeed, still have not been conducted, since the concrete participants of the leading reaction and the temperature of its flow are unknown.

The actual idea about the fact that the first stage of burning of volatile explosives is the transformation of them into pairs is absolutely indisputable and even inevitable in the case of such substances as, for instance, methylnitrate, boiling at 66° without noticeable decomposition, or even more, solutions of liquified gases, boiling at very low temperatures. Such a phase mechanism of burning is real, as Belyayev showed, and for substances with comparatively high temperatures of boiling, such as nitroglycol, nitroglycerine, tetranitrate, tetryl and others. In those conditions the burning speed of the heating of the substance is so great that it is evaporated before a chemical reaction occurs to a noticeable degree.

2. Burning of Explosives in the Presence of an Exothermic Reaction in the Condensed Phase

The boiling point increases with an increase of pressure. The higher pressure, under which burning of volatile explosives occurs, the higher the temperature of the layer of the substance adjacent to the surface is heated. When the pressure is sufficiently high, the temperature of the heated layer can be raised so that the speed of the reaction of decomposition of the explosive in condensed phase will become noticeable as compared to the speed of evaporation. This should lead to an increase of the burning rate, since the part of heat, separated into the condensed phase will be transmitted to neighboring layers by thermal conduction directly by a liquid or solid, but not through a layer of vapor, as there is room under conditions when the reaction and liberation of heat occur only in the gas phase. In the case of nonvolatile explosives a type of nitrocellulose reaction occurs in the condensed phase and at low pressures. Certain regularities of the burning of explosives in the presence of exothermic reaction in the condensed phase differ from those, which give the above considered theory.

The process of burning of nitrocellulose, and also powders on its basis, can be presented in the following form (Fig. 4.25).

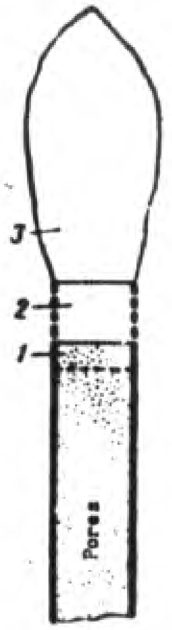

Fig. 4.25. Diagram of burning of nitrocellulose or powder. 1 — zone of exothermic reactions in condensed phase, 2 — zone of flameless exothermic reactions in gas phase, 3 — zone of flame.

Weak-exothermic reactions are the first stage which occurs in the condensed phase with formation of gaseous products (zone 1). The speed of reactions in the condensed phase, as well as the burning rate (if the reactions under the given conditions are leading ones), should not depend on pressure. Actually, as P. F. Pokhil showed, the burning rate of pyroxylin and nitroglycerine powders at very low pressure (up to 40 mm of the mercury column) does not depend on the pressure.*

Gaseous products of reactions of the first stage enter into a reaction with each other (zone 2). Reactions of this second stage, apparently, are bimolecular, flow also with the liberation of heat and also lead to the formation of intermediate substances capable of reaction, but relatively more difficult to entering into a reaction (NO, CO and others). Since a reaction in zone 2 is exothermic, then the temperature obtainable in it is higher than during reactions in the condensed phase. Products of reactions of the first stage possess a high reactivity, therefore, a reaction of the second stage with pass small activation energy, in other words, their speed

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*Experiments were produced with strongly heated powders, since in usual conditions (small diameters of cartridge, room temperature) powders at such low pressures in general do not burn.

weakly depends on the temperature.

In this includes the essential distinction of the process of burning of nitrocellulose, powders on its basis and other nonvolatile explosives from that procrss, which is considered in the theory of Belyayev-Zel'dovichfor volatile substances. In the latter case it is considered that activation energy is of the leading reaction E >> RT. This assumption allows that the reaction basically flows in narrow zone at a temperature, close to the maximum. Here the reactions of the second stage are stretched on the entire extent of zone 2 (see Fig. 4.25). The basic factor, affecting their passage, is pressure.

Finally, at heightened pressure exothermic reactions of the third stage begin to flow strongly, accompanied by the appearance of a flame, by which nitrogen oxide is reduced to basic nitrogen (zone of flame 3).

During stationary burning the speeds of all three stages, obviously, are identical.

The speed of a reaction in the condensed phase depends on the temperature at which it flows. At very low pressures this temperature is determined only by the thermal effect of the reactions of the given stage. If the pressure is high, then zone 2 grows, since the speed of reactions of the second stage increases; they flow then nearer to the surface of the condensed phase and their heat is partially transmitted to the condensed phase, increasing its heating up. This increases the speed of reactions of the first stage and consequently also the burning rate. Thus, in that region of pressures, in which heat, separating into zone 2 noticeably increases the temperature of the condensed phase, the burning rate becomes depending on the pressure.

If pressure is even higher, then it goes into flame reactions (zone 3). In the zone of the flame the temperature is strongly increased and correspondingly heat from it can be transmitted to the zone of reactions of the second stage and even further – to the zone of reactions of the first stage. The temperature of the condensed phase is increased and correspondingly the flow of reactions is accelerated.

The influence of reactions of the third stage on the burning rate depends on the pressure. With a pressure, at which only a flame appears, the influence of the flame on the burning rate still does not appear. This is explained by the fact that the distance between the flame and the surface of the explosive is great and heat from the flame practically does not reach it. With a further increase of the pressure of zone 2, which separates the surface of the explosive from the flame, the pressure will become even higher, the more heat is transmitted from zone 3 to zone 2, and from it to zone one. With large pressures the influence of reactions of the third stage becomes predominant. In these conditions the dependence of the burning rate of powder from its heat of combustion appears.

Thus, at low pressures of conducting, the reaction is in condensed phase, at high flame reaction, at intermediate pressures the burning rate is determined by the totality of the reactions of all three stages.

The described system of burning of nitrocellulose should be considered as simple. In reality, as was assumed earlier, and Pokhil showed experimentally, during burning, at least in the region of low pressures, there is a dispersion of the burning substance. It is caused by the fact that decomposition in the surface layer of the condensed phase occurs nonuniformly and the forming separate bubbles of gas detach and attract particles of the substance. A pressure of about 2 mm, only 30% of pyroxylin powder is turned into gasses, but 70% of it is turned into smoke, constituting practically the unchanged powder. At burning under higher pressures (up to 100 mm) the quantity of smoke decreases, its composition is also changed in the direction of enrichment by carbon and lack of nitrogen and oxygen.

3. Burning of Quick-Burning Explosives

Mechanisms of burning of certain quick-burning explosives, for instance, mercury fulminate and volatile substances are qualitatively distinguished. In the first case to an even greater degree than for nonvolatile secondary explosives, there is room for dispersion of the surface layer of the substance and it passes in the form of dust by the flow of gases from the surface of the condensed phase, which continues to react. The reaction is completed, at least low pressures, at a significant distance from the front. Inasmuch as the surface of the heat exchange between the products of burning and the dispersed substance is very large, the quantity of heat obtained by the substance per unit of time is much more than in the above considered cases, when dispersion is lacking or it is small and the surface of heat exchange is close to the area of the cross section of the cylindrical charge. The burning rate is also correspondingly much greater (dozens of times).

The dependence of the burning rate on the pressure (at low pressures) has the same form as during burning of usual type explosives.

However, with an increase of pressure the dependence of the burning rate on pressure is changed (Fig. 4.26). In the case of mercury fulminate the growth of speed is delayed, and within a wide interval of pressure the speed is expressed no longer as a linear function of pressure, but by the relationship

$$u=A+Bp^{\nu}.$$

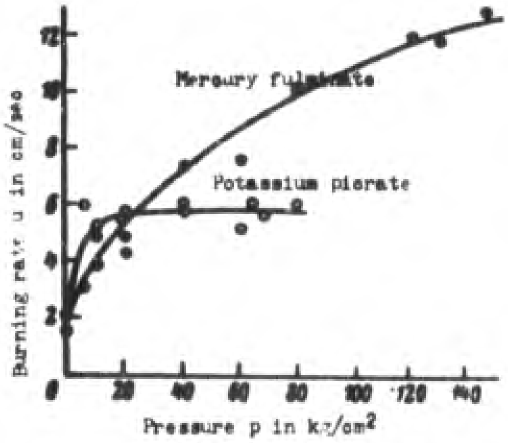

Fig. 4.26. Dependence of the burning rate of mercury fulminate and potassium picrate on the pressure.

where A = 1; B = 1.04, ν = 0.5 (and is expressed in cm/sec, p — in kg/cm^2).

The dependence on pressure of the burning rate of potassium picrate is changed even more sharply; up to 4 kg/cm^2 the speed increases rapidly, and then for a large interval the change of pressure remains constant.* A weak dependence of the burning rate on pressure was observed also for certain other quick-burning and slow-burning explosives. Thus, according to Suetlov and Fogel'zang for strongly pressed lead styphite, the burning rate of which is very great, it hardly increases with the pressure, remaining practically constant (33-34 cm/sec) during its change from 150 to 400 kg/cm^2. With a decrease of pressure from 150 kg/cm^2 to 15 mm of the mercury column the burning rate decreases very little — approximately to 25 cm/sec.

The independence of the burning rate on pressure, apparently, is connected with the fact that in corresponding conditions of the fastest of consecutive stages and therefore the leading reaction in the condensed phase becomes exothermic. The speed of this reaction cannot depend on the pressure.

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*As the latest research has shown, the dependence of the burning rate of potassium picrate on the pressure is more complicated: from 4 to 60 kg/cm^2 significant deceleration is observed; at a further inincrease of pressure up to 400 kg/cm^2 it remains constant.

§ 7. Unstable Burning of Explosive Substances

1. Gas-Dynamic Conditions of the Stability of Burning

Experience shows that burning of secondary explosives preserves a uniform character and constant speed only with certain conditions. Thus, the uniformity of burning of a powdered explosive of small density is disturbed with an increase of pressure. Starting at a certain pressure, depending on the density and properties of the explosive, burning is sharply accelerated, becomes pulsating and can even pass into detonation.

Liquid explosives show a similar behavior. Starting from a certain limiting pressure different for various liquids and conditions, burning also loses uniformity, becomes pulsating and is sharply accelerated.

Initiating explosives are especially inclined to unstable burning with transition to detonation. Some of them, for instance lead azide, at all studied conditions elusively fast pass from burning to detonation, others, as, for instance, mercury fulminate, although capable in certain conditions (large density of powder, burning of the cartridge without a shell) do stationary burning, but during the majority of conditions, in which secondary explosives burn stably, also rapidly pass from burning to detonation.

The characteristic of the stability of burning can be given on the basis of the following considerations. During burning an explosive is turned into gases. Since the density of gases, especially at high temperatures of burning, is very small as compared to the density of a solid, the products of burning are strongly expanded, going moreover into motion. It is obvious that gases go into motion at the expense of a certain increase of pressure above the surface of burning of the explosive. However, the appearance of increased pressure leads to an increase of the burning rate which in turn accelerates the motion of the gases.

In order to establish the final result of these two phenomena, it is necessary to consider their reaction quantitatively.

As a simple case we will consider burning with one open face of a cylindrical charge of an explosive in a durable tube with a section 1 cm^2 with an external pressure p_0. The forming gases flow in the direction, opposite the direction of the propagation of burning, with a speed, depending on the speed of their formation (Fig. 4.27). We will present graphically processes of the formation of gases during burning and expiration of them from the tube depending on the pressure inside the tube.

In Fig. 4.28 along the axis of the abscissas is plotted the pressure at the surface of the explosive. Along the axis of ordinates are plotted the values: m_1 – quantity of gases forming at a given pressure per second per cm^2 of the surface of the front (mass burning rate), and m_2 – quantity of gases, ensuing per unit of time at the pressure inside the tube p and external pressure p_0 for each square centimeter of section of the tube (gas bleeder).

It is obvious that according to the law of preservation of momentum

$$p-p_0=m_1u_г.$$

[г = g = gas]

Here u_g is the exhaust velocity of gaseous products of burning, where

$$u_г=\frac{m_1}{\rho_г},$$

where ρ_g is the density of the gases.

Then

$$p-p_0=\frac{m_1^2}{\rho_{\text{г}}}.$$

The line of the gas bleeder m_2 depending on the pressure has, as known from gas dynamics, the form depicted in Fig. 4.28. With $p = p_0$, i.e., when the pressure above the surface of the explosive is equal to the external pressure, the drain of gas is equal to zero. By increasing the pressure the drain of gases is increased, wherein at the beginning this increase goes by a curve,* and then, starting with a pressure approximately twice exceeding the external, the drain of gases m_2 increases directly proportional to the pressure,

$$m_2=Kp, \tag{4.23}$$

where K is a constant, depending on the temperature, density, and heat capacity of the gases.

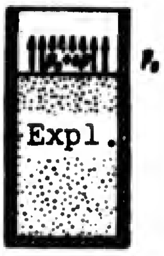

Fig. 4.27. System of outflow of gases during burning of an explosive in a tube.

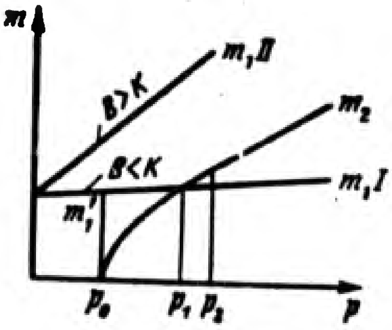

Fig. 4.28. Dependence of gas influx m_1 during burning and gas bleeder m_2 on the pressure.

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*The equation of this curve has the form:

$$m_2=\sigma\left(\frac{p_0}{p}\right)^{\frac{1}{k}}\sqrt{\frac{2k}{k-1}p\rho_{\text{г}}\left[1-\left(\frac{p_0}{p}\right)^{\frac{k-1}{k}}\right]}.$$

where σ is the section of hole for the exit of gas;

k is index of adiabat;

ρ_g is density of gas at pressure p.

Line of incoming gas in our conditions is essentially a line depicting the mass burning rate as a function of pressure,

$$m_1 = u_м.$$

[м = m = mass]

Considering in accordance with the given experiment that

$$u_м = A + Bp. \qquad (4.24)$$

we will construct in Fig. 4.28 for m_1 two straight lines in conformance with various values of B: a straight line I for the case, when $B < K$, and straight line II – when $B > K$.

In the case, when $B < K$, the line of incoming gas intersects the line of the gas bleeder, and burning, as it is easy to show, will be stable. Really, if we light an explosive at p_0, then with this pressure the gas bleeder is equal to zero, but incoming gas is depicted by the ordinate m_1' (see Fig. 4.28). At the expense of the difference of incoming gas and the gas bleeder, the pressure for the front of burning will increase as long as pressure p_1 is not attained, at which the gas bleeder becomes equal to the incoming gas. With $B < K$ the pressure is not able to increase farther, since with $p > p_1$ the expenditure of gas is greater than incoming gas. Therefore, if the pressure by any accidental cause was increased, for instance to value p_2, it inevitably then must be lowered to value p_1.

By means of analogous reasoning, it is easy to show that with $B > K$ (straight line II on Fig. 4.28) the pressure in the tube will continuously increase which with corresponding conditions can lead to the appearance of detonation.

Thus, the possibility of stable burning at a given pressure is determined by the relationship between the burning rate (to the more exact, the speed of gas forming) and the speed of the drain of gases at this pressure or, speaking more correctly, the relationship between the speed of increase growth of incoming gas and the speed of increase of the gas bleeder with pressure.

If during equality of incoming and exiting gas first grows with a pressure faster than the second, then burning is unstable, and, conversely, if incoming gas increases slower than exiting gas, then stable burning will occur. The stability of burning should be determined by the relationship of the magnitudes: K — the tangent of the angle of inclination of the straight line of exiting gas and B = $= \frac{du_m}{dp} = \frac{dm_1}{dp}$ — the derivative of the burning rate (more exactly, the speed of gas formation) by pressure. The limit between the regions of stable and gas-dynamically unstable burning is determined by the condition

$$B=K \text{ with } m_1=m_2.$$

Inasmuch as those or other parameters (for instance, pressure, temperature, density of explosive) affect the magnitudes of B or K, they will also influence the stability of burning.

On the basis of these general gas-dynamic considerations about conditions of the stability of burning available data in reference to specific explosives and conditions of burning will be considered.

We will calculate first the value of K — proportionality factor between exiting gas and the pressure. From gas dynamics it is known that

$$K=\sigma\psi_{\max}\sqrt{\frac{2gT_0}{p_0T_1}}. \qquad (4.25)$$

where σ — section of the hole for exit of gases,

$\psi_{max} = \left(\frac{2}{k+1}\right)^{\frac{1}{k-1}}\sqrt{\frac{k}{k+1}}$; with K = 1.41 for diatomic gases $\psi_{max} = 0.484$;

ρ_0 — density of products of burning at normal conditions;

T_1 — temperature of gases.

From the expression (4.25) it is clear that the coefficient K is not strictly constant for all explosives, and can be changed accordingly with different possible values of heat capacity, temperature, and density of gaseous products of burning.

We will calculate the value of the coefficient K, taking for simplicity that the temperature of burning is equal to 2730°K, and the density of gases is $1.25 \cdot 10^{-3}$ g/cm^3 (carbon and nitrogen oxide). Under these conditions the coefficient K ≈ 7.4 g/cm^2 sec:kg/cm^2.

For an appraisal of the stability of burning it is necessary to compare this value K with the value of $\frac{du_m}{dp}$ from the expression of the dependence, of the burning rate on pressure ($u_m = A + Bp$). Inasmuch as this dependence, as experiment shows, in certain conditions of burning is linear, the derivative $\frac{du_m}{dp}$ is a constant, which we have designated B. The values of the magnitude of B are given in Table 4.12.

As can be seen, for all studied secondary explosives the value of the magnitude of B is 50-200 times less than the value of K. Thus, the ability of secondary explosives to stable burning theoretically is completely natural.

Those initiating explosives, which in a pressed to a very high density state are able to burn stably, give a linear dependence of the burning rate on pressure, as well as secondary substances, but the value of B for them is much larger than for secondary, and near to the limit. It is possible to assume that those initiating explosives, for which stable burning was not observed experimentally, are characterized by even larger values of the magnitude of B,* which should lead to the disturbance of the equilibrium between incoming gas and exiting gas, in other words, to the impossibility of stable burning.

Thus, one of fundamental facts — the stability of burning of secondary explosives and the combustion instability of initiating explosives is explained by the theory.

Table 4.12. Value of the Coefficient B in the Formula $u_m = a + Bp$ for Various Explosives

Explosive	Pressure interval in atm (tech.)	Values of the magnitude of B in $g/cm^2 sec.kg/cm^2$
Trotyl	40—1000	0,00675
Picric acid	40—1000	0,00786
Tetryl	200—1000	0,0101
Hexogene	30—500	0,0270
Collodion	5—30	0,0162
Pyroxylin No. 1	3—12	0,0405
Tetranitrate	15—500	0,0193
Liquid methylnitrate	0,2—1,5	0,133
Liquid nitroglycol	1—12	0,0390
Gelatin nitroglycol	1—150	0,0315
Gelatin nitroglycerine	0,5—2,2	0,146
Mercury fulminate	To 1	4,18
Trinitrotriazidobenzene	To 1	0,85

It is known, however, that secondary explosives, burning in most cases stationary and stably, in certain conditions of burning (for instance, with significant porosity or in a liquid state) give the transition of burning to detonation. In exactly the same way those initiating explosives, which according to the theory have to burn

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*The case of burning with very great speed and at weak dependence of the burning rate on the pressure is possible (in the formula $u_m = A + Bp$ the magnitude of A is very great, and of B — small). In this case during igniting a large dynamic increase of pressure can occur, just as with a large B.

stably and indeed burn so in certain conditions (for instance, in a strongly pressed state, in a vacuum), in other conditions (for instance, at smaller pressures of pressing) give rapid transition of burning to detonation.

From the point of view of the theory of transition of burning to detonation, both cases should be interpreted as a result of the change of the dependence of speed of incoming gas on the pressure in the direction of the increase $\frac{dm_1}{dp}$. The question appears, why and how is this change accomplished? For the answer to this question experimental data on burning of powdered and liquid explosives in those conditions, when the stationary flow of the process is disturbed and the theoretical interpretation of this disturbance will be considered.

2. Unstable Burning of Powdered Explosives

Burning of solid powdered explosives goes evenly and stably not at all conditions. If the pressure exceeds a certain limit, the magnitude of which depends on different factors and in the first place on the density, then the dependence of the burning rate on the pressure is changed. Thus, for pyroxylin No. 1 with a density of 0.37-0.45 g/cm^3 the linear law of the growth of speed with pressure is executed only to a pressure of ~3 kg/cm^2 (Fig. 4.29). At pressures from 3 to 4 kg/cm^2 the speed grows somewhat faster, but burning still preserves a uniform character. Starting from a pressure near 4 kg/cm^2, burning becomes jerking, pulsating, the total time for burning a section of given length sharply decreases.

It is natural to assume that a change of conditions of burning with an increase of pressure is caused by penetration of gaseous products of burning to the thickness of the powder. The consequences of this phenomenon depend on the speed of penetration of the gases.

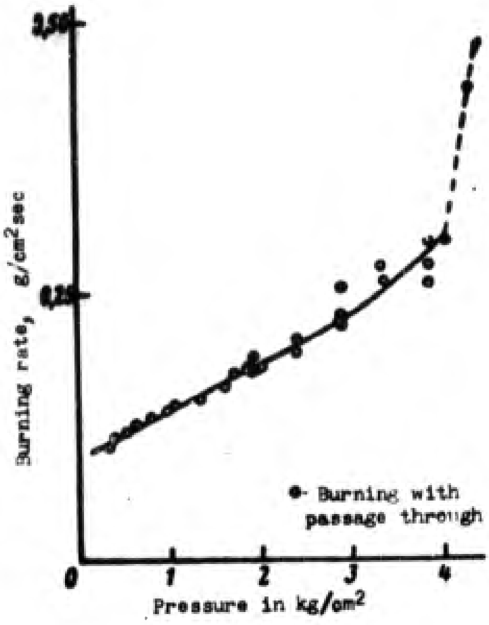


Fig. 4.29. Dependence of burning rate of pyroxylin No. 1 of low density on the pressure.

If the speed of penetration of the gases does not exceed noticeably the burning rate, then the time necessary for penetration of gases through a layer of a given thickness, and burn-up time of this layer, are close. The influence of the penetration of gases in this case is limited only to a certain increase of the surface of burning without evident disturbance of its uniformity. Since the depth of penetration of gases is increased with the growth of pressure, then the burning rate in the presence of this phenomenon increases with pressure faster than in its absence.

At great speed and depth of penetration gases outstrip the front of burning and embrace the layer of powder of noticeable thickness. This layer then burns fast, especially, if a particle before ignition succeeded to be heated. The gases flowing in this case can attract unreacting particles of explosives. Such a combustion, similar to a flash, will accompany a certain increase of pressure, strengthening the penetration of gases to the depth of the powder. Development of this phenomenon can lead to the appearance of detonation.

However, such a case is possible, when after an increase of pressure due to burning out of the heated layer its decrease follows, which in certain conditions leads even to damping. In other conditions, burning does not dampen, and is only delayed, then it accelerates again at the expense of the penetration of gases in pores of the explosive and the cycle is repeated. In this case, the amplitude of oscillations of the pressure does not reach the limit leading to the appearance of detonation. Burning continues to the end, but in pulsating conditions.

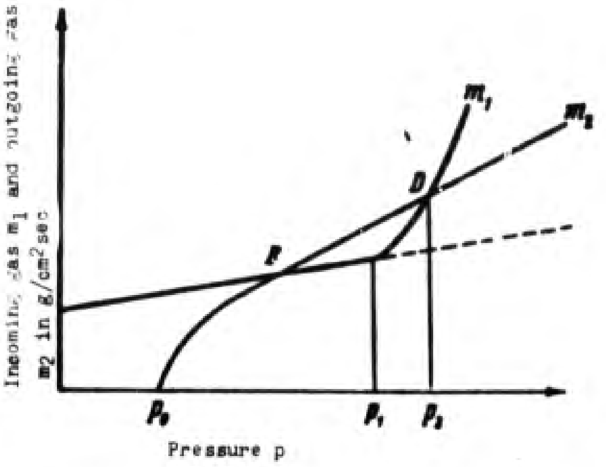


Fig. 4.30. The influence of pressure on the stability of burning of powdered explosives.

Self-accelerated burning of a porous explosive can be presented by graph (Fig. 4.30). Up to pressure p_1, the magnitude of which depends on the density and dimensions of the particles of the powder, the burning rate and, consequently, incoming gas slowly and linearly grow with the pressure, where the tangent of the angle of inclination of the straight line of incoming gas is less than the straight line of exiting gas.

With a further increase of the pressure the derivative $\frac{dm_1}{dp}$ increases, the line of incoming gas deviates upwards at the expense of penetration of gases to the depth of the powder and with a pressure of p_2 again intersects the straight line of exiting gas. At point B the derivative of incoming gas is by the pressure $\frac{dm_1}{dp} < \frac{dm_2}{dp}$, and at point D the derivative is $\frac{dm_1}{dp} > \frac{dm_2}{dp}$.

In both points incoming and exiting gases are in equilibrium, however, it is easy to show that at point B this equilibrium is stable, and at point D — unstable and the least increase of pressure will evoke an excess of incoming gas over exiting gas and further progressive growth of the pressure and burning rate.

Thus, by itself the presence of porosity, more exactly gas-penetrability, does not necessarily lead to disturbance of the stability of burning. Burning becomes unstable, when pressure exceeds the limit, the magnitude of which, other things being equal, is even greater the lower the gas-penetrability of the substance. Thus, burning of powdered nitrocellulose even with a small density can at low pressures flow by parallel layers and at the same speed, as burning a powder prepared from it.

The basic cause of the penetration of gases to the depth of the powder, undoubtedly, is the dynamic increase of pressure Δp on the front of burning, corresponding to that momentum, which the flowing gases obtain. The value of Δp grows with an increase of pressure, inasmuch as with this the burning rate is increased. Therefore, the influence of the penetration of gases in pores can be lacking at burning under small constant pressures and appear with large pressures.

A still more favorable condition for penetration of gases is during burning in a closed volume under increasing pressure. Experiments have shown that in these conditions a decrease of the density of a powdered explosive sharply strengthens the inclination of burning to a transition to detonation. Thus, hexogene with a density, equal to 0.9 specific gravity, does not detonate during burning even in a durable shell (pressure of burst is 700 kg/cm^2), at the same time in the form of a powder of small density hexogene gives a transition of burning to detonation in a shell, bursting at 45 kg/cm^2.

3. Unstable Burning of Liquid Explosives

Burning of all studied in this respect liquids — methylnitrate, nitroglycol, nitroglycerine, diglycoldinitrate — occurs evenly only at certain conditions. The basic of these conditions are pressure, temperature, and viscosity of the liquid. Outside the region of the "normal" burning line, which expresses the burning rate as a function of pressure, it is bent upwards similarly as this is observed in the case of powdered explosives (see Fig. 4.30).

The change of character of burning of liquid explosives during certain conditions was predicted by L. D. Landau. He showed that normal "thermal conduction" conditions of burning, occurring in the evaporation of a liquid, heating, and chemcial reaction in vapors, is, speaking generally, unstable. Accidental perturbation of the surface of burning the liquid attempts to increase by amplitude in time. The greater the speed of propagation, the less the stability of the flat front of burning. Factors, stabilizing the surface of a liquid and preventing distortion of the front are gravity, surface tension, and viscosity of the liquid. Flame stabilization can be ensured also by small diameter of tube.

Disturbances of normal conditions of burning of liquid explosives are expressed in a turbulence of the front of burning, which lead to an increase of the quantity of substance, burning per unit of time, per unit of area of the section of the column of the liquid.

The maximum terminal velocity, at which burning can still remain undisturbed, is determined, according to Landau, by taking into account the stabilizing influence of gravity and surface tension by the equation

$$u_{\text{м}\,\max}=(4\alpha_{\text{к}}g\rho_{\text{г}}^{2}\rho_{\text{ж}})^{1/4}, \qquad (4.26)$$

[к = b = boiling; ж = li = liquid]

where $u_{m\ max}$ is the critical mass burning rate in g/cm^2 sec;

α_b is the surface tension between the liquid and its saturated vapor at the boiling temperature;

ρ_g is the density of gaseous products of burning;

ρ_{li} is the density of the liquid.

According to V. G. Levich in cases when the viscosity of the liquid is great or the surface tension is small, the stabilizing influence of the viscosity predominates. The limiting value of the burning rate is determined in such cases by the relationship

$$u_{м\,\max}=(3\sqrt{3}\,g\eta\rho_г^{2}\rho_ж^{1/3})^{1/3}, \qquad (4.27)$$

where η is the viscosity of the liquid.

The expression (4.26) can be converted, using an approximate relationship for the parachor P

$$P=\frac{M\sigma^{1/4}}{\rho_ж}, \qquad (4.28)$$

where M is the molecular weight of the explosive.

Then for the critical mass speed is obtained

$$u_{м\,\max}=7,91\,\frac{P}{M}\,\rho_г^{1/4}\rho_ж^{3/2}. \qquad (4.29)$$

Use of this formula (although somewhat less exact) for the characteristic of the stability of burning is especially convenient because the parachor can be calculated by the structural formula of the substance and does not change depending on the temperature within a wide interval of change of the latter. Furthermore, the formula allows appraisal of the influence of the chemical structure of the liquid explosive on the stability of burning and shows that the value of terminal velocity for different explosives is changed within very narrow limits.

Really, the P/M factor physically corresponds to the specific volume of the substance at a temperature, at which $\alpha_b = 1$, and the magnitude of it oscillates for various explosives in narrow enough limits. The same pertains also for other magnitudes, entering in the right part of the formula, which can be considered as approximately constant. As calculations show, this magnitude constitutes approximately 0.25 g/cm^2 sec at atmospheric pressure.

Inasmuch as the terminal velocity for various explosives are approximately identical, the stability of normal burning can be characterized by the magnitude of the actual burning rate at given conditions of pressure and temperature.

Formulas (4.26), (4.27), or (4.29) give the dependence of terminal velocity on the pressure, under which burning occurs. During a change of pressure the right part of the formulas changes basically only by the density of gases proportional to the pressure. Considering this dependence, we obtain

$$u_{m\,\max}=\beta p^{1/2}, \qquad (4.30)$$

where $\beta \approx 0.25$, if p is expressed in kg/cm^2, and u_m – in g/cm^2 sec.

Thus, the condition of stability of normal burning of a liquid can be formulated by the following form: if the burning rate at a given pressure is more than $\beta p^{1/2}$., then the burning is unstable and vica versa.

Since the burning rate, as we have seen, with an increase of pressure grows proportional to p, and the terminal velocity according to (4.30) is increased proportional to $p^{1/2}$, then it is obvious that with an increase of pressure the stability of burning decreases.

The considered relationships maintain their accuracy only as long as the pressure, under which the burning occurs, is not too close to the critical pressure, and the boiling point according – to the critical stagnation temperature for the given substance. During critical conditions the surface tension of the liquid becomes equal to zero, and according to the expressions (4.26) or (4.29) also the value of terminal velocity should fall to zero. Inasmuch as the critical pressure of organic liquids, the experiment shows, is almost 50 atm (tech.), then hence the conclusion can be made that the normal burning of liquids higher than 50 atm (tech.) is impossible, if only their viscosity is insufficient in order to stabilize the burning according to the expression (4.27).

Therefore, if with an increase of pressure near the critical pressure, the burning rate should at the expense of the effect of Landau grow faster than at smaller pressures; furthermore, pulsation should appear. These circumstances do not exclude, however, the possibility of preservation in the transition region of the character of burning, and during a small period of pulsation — even its apparent uniformity.

Formula (4.29) also shows the influence of initial temperature of an explosive on the stability of its normal burning. The limiting burning rate is practically independent of temperature; more exactly, it decreases very slightly with a rise in temperature corresponding to a decrease in the density of the liquid. At the same time, the burning rate increases with temperature; this indicates that the stability of normal burning should decrease with a rise in the initial temperature.

However, in the influence of pressure and temperature there is a difference. Pressure can be increased without limit, up to values, corresponding to the disturbance of normal conditions of burning of any liquid; the possibility of the increase of temperature is limited by the temperature of self-ignition of the substance. Therefore, it is not possible for any liquid explosive by means of increasing the temperature to arrive at a disturbance of the stability of burning.

A comparison of experimental data limiting the pressure, at which conditions of uniform burning for number of explosives is disturbed, showed good agreement with the theory. For nitroglycerine this pressure was almost 0.5 atm (tech.), for methylnitrate — almost 2 atm (tech.), for nitroglycol — nearly 20 and for diglycoldinitrate — nearly 50 atm (tech.).

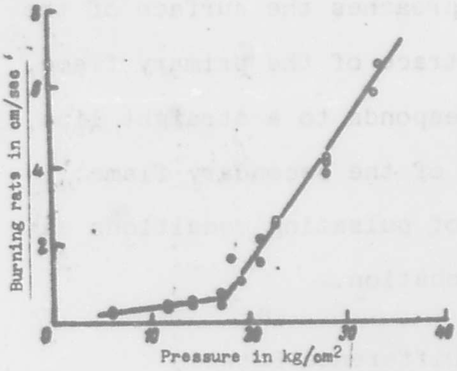
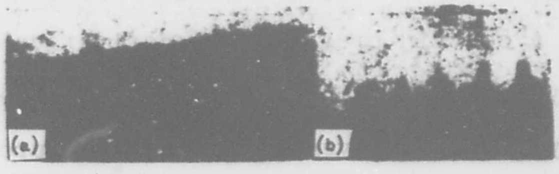


Fig. 4.31. The influence of pressure on the burning rate of nitroglycol.

Also (on gelatin liquids) the influence of viscosity on the stability of burning was studied; it was determined that the stabilizing influence of viscosity quantitatively corresponds to the theory.

It is necessary to add that the transition to an unstable region usually leads to burning a pulsating condition, which proceed with a speed exceeding the speed of undisturbed burning by a few times. Figure 4.31 shows the change of the burning rate of nitroglycol at pressures, lying below and above the limit of the transition to a region of unstable conditions. In both cases speed grows with pressure linearly, but in the last case — much faster.



GRAPHIC NOT REPRODUCIBLE

Fig. 4.32. Photograph on moving film of burning at 16 atm (tech.) of gelatin nitroglycol (a) and non-gelatin (b).

Figure 4.32a, gives a photograph on moving film of the burning of gelatin nitroglycol at 16 atm (tech.). The burning goes evenly, and in the photograph two flames are distinctly conspicuous: the primary — in the form of a narrow line and at certain distance from it — a wide bright secondary flame.

Burning of liquid non-gelatin nitroglycol (Fig. 4.32b) with those same conditions goes with intense pulsation. A secondary flame in the form of separate tongues at times approaches the surface of the liquid and then is rejected from it. A trace of the primary flame, weakly distinctive on the positive, corresponds to a straight line, connecting the lower ends of the tongues of the secondary flame.

In known conditions the appearance of pulsating conditions can lead to the transition of burning to detonation.

4. The Physical Basis of the Difference Between Initial, Secondary, and Launching Explosive Substances

Analyzing the peculiarity of the process of burning in reference to the above considered conditions (burning in cylindrical tube on an end, see Fig. 4.27), it is possible to construct a general system of the influence of different factors, in the first place the pressure, on the stability of burning of solid (porous or nonporous) and liquid explosives. Let us consider for that the different possible relationships of incoming gas and exiting gas (Fig. 4.33a, b, c).

Starting with a certain pressure the derivative of the quantity of flowing gases by pressure has a constant magnitude for given explosives (more exactly, for the given composition of products of burning and their temperature). If the initial section in the region of small dynamic increases of pressure is disregarded, then the line of exiting gas can be represented by a straight line, the continuation of which passes through the origin of the coordinates (OB).

In the region of small pressures the line of incoming gas constitutes a straight line for nonporous, as well as for porous and liquid explosives. However, at heightened pressures only for nonporous solid substances (line 1) does it remain a straight line and preserves its slope to the axis of the abscissas. If with this the straight line of incoming gas has a slope less than the straight line of exiting

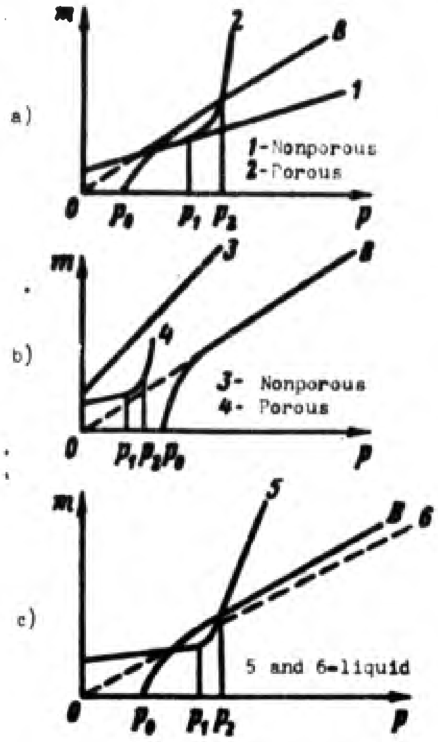


Fig. 4.33. The influence of pressure on the stability of burning of different explosives.

gas, then the pressure at the surface of the front remains constant during a given external pressure and only somewhat exceeds the latter. According to the constant, a burning rate remains which is stable. Substances with such characteristics of the burning rate are secondary explosives (see Fig. 4.33a). If the angle of inclination of the straight line of incoming gas at the axis of the abscissas (line 3) is greater than the angle of inclination of the line of exiting gas, then the pressure for the front increases and the burning can be accelerated up to detonation. Substances with such characteristics of the burning rate are typical initial explosive substance (see Fig. 4.33b), which preserve these properties even with the maximum possible density of the charge.

For porous substances the stability of the burning depends on their gas penetrability: starting from a certain pressure p_1, which depends on the density and properties of the substance, the speed of incoming gas starts to increase due to penetration of gases in the depth of the explosive and with that more acutely the higher the pressure (curves 2 and 4). At a certain pressure p_2 the lines of incoming gas cross, where $\frac{dm_1}{dp} > \frac{dm_2}{dp}$. Pressure at the surface of the burning explosive, which before this was only a little greater than the external pressure, starts rapidly to increase, as a result of which burning is accelerated and can even go into detonation.

If p_2 is less at 1 atm (tech.), then we carry the explosive to the number of initial explosives (curve 4). With p_2, greater than 1 atm (tech.), – to the number of secondary explosives (curve 2).

The distinction in behavior of secondary and initial substances is caused by the fact that the burning rate of initial substances is so great that in the case of free burning at atmospheric pressure the increase of pressure at the surface of the burning explosive is enough so that gases can penetrate the pores and stable burning becomes impossible. The burning rate of secondary substances at atmospheric pressure is insufficient for that and the shown effect is not observed, it appears during burning under increasing or under constant, but sufficiently high pressure.

The gas-dynamic increase of the pressure in the front grows with the burning rate, which rapidly increases with the pressure. It follows from this that the higher the pressure, at which burning goes, the greater the increase of the pressure in the front. When external pressure becomes higher than a definite magnitude (which depends, in particular, on the dimension of the pores), penetration of gases to the depth of the substance begins.

In the case of liquid explosives (see Fig. 4.33c) the acceleration of incoming gas with an increase of pressure occurs after achievement of a certain critical value of the burning rate due to the appearance of the Landau effect. When the slope of a curve of incoming gas (line 5) becomes greater than the slope of the straight line of exiting gas, acceleration of burning sets in with favorable conditions for detonation. In the absence of such conditions burning maintains stability and also with large pressures (line 6).

If the critical speed and the speed, which corresponds to the condition $\frac{du_m}{dp} > K$, attained at a pressure less than atmospheric, then the liquid explosive is initial. An example of such an explosive is nitrogen chloride and hydrazoic acid. If critical speed is attained at a pressure higher than atmospheric, then the liquid explosive is secondary. An example of such a liquid explosive is methylnitrate and nitroglycol.

Thus, the idea of "initial explosives" and "secondary explosives" are conditional. The basic parameter for separation of these classes of explosives is the burning rate at atmospheric pressure. If this speed is sufficiently small, so that the effect of penetration of gases to the depth of the substance is lacking, then such a substance is secondary; conversely, if this penetration is expressed so strongly that burning passes very rapidly to detonation, then the substance is initial.

These considerations also explain the phenomenon "repressed" initial explosives, which have more or less completely lost the ability to give rapid transition of burning to detonation.

The phenomenon of repressing is observed for such initial explosives, for which the magnitude B in the equation (4.24) although great, has less critical value. The burning rate at atmospheric pressure is correspondingly great which leads to a noticeable dynamic increase of pressure for the front. However, in the absence of pores or insignificant porosity, remaining in strongly pressed explosives, this increase of pressure gives only a certain increase of the burning rate above that value, which corresponds to the external pressure. If, however, the substance has significant porosity, as this usually occurs during technical use of moderately pressed initial explosives, then under the influence of the increase of pressure in the front gaseous products of burning penetrate into the depth of the substance, the actual surface of burning is increased and the speed of gas forming per unit of area of the section of the charge becomes a greater limit, allowing stable burning. In these conditions appearing during ignition, burning even at atmospheric pressure very quickly passes to detonation as is required from initial explosives. Therefore, in capsule-detonators mercury, fulminate and similar to initial explosives are pressed only under moderate pressures, which give a density, comprising only about 2/3 specific gravity.

In the light of the latest research the considered gas-dynamic treatment of the transition of burning of initial explosives to detonation should be considered a correct, but not exhausting phenomenon.

The latest research has shown that the burning rate of mercury fulminate and several other quick-burning explosives grows strongly with pressure only with relatively small pressures; with a further increase of the pressure the growth of speed is delayed or even ceased which makes burning of the gas-dynamic stable. Furthermore, an increase of pressure due to exceeding incoming gas above exiting gas may be, apparently, comparatively slow and it is doubtful whether it is in a state to lead to the appearance of a sharp change pressure, characteristic for detonation.

It is possible to imagine another way of the appearance of a sharp change of pressure. During igniting of an explosive as a result of dispersion a layer of a dustgas suspension from particles of the explosive and gaseous products of incomplete combustion will be formed.

In order to burn the initially formed dust particles of the explosive, a certain time is required, the larger the dimension of the particles the more time required. During that time dispersion continues to spread and the thickness of the layer of the suspension is increased. When the thickness of layer attains a certain critical value, in it, as a result of the dynamic increase of pressure* or by

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*The sections of tube, through which the gases pass, remains as constants, and the effective surface of burning increases.

thermal mechanism,* an explosion appears. The explosion of a sufficiently thick layer of a suspension evokes detonation of the explosive. It is natural that a small density explosive, facilitating penetration in it of gaseous products of burning, promotes formation of a layer of a dustgas suspension of the critical thickness.

We established the essence of the distinction between initial and secondary explosives.

We will consider the distinctive peculiarities of launching explosives, or powders.

Powder by its own chemical nature constitutes secondary explosives, such a physical structure which the stability of burning of them is significantly higher than secondary explosives in their usual state is a liquid or crystal powder.

We saw that secondary explosives with their small coefficient of acceleration of burning B, in general, have to burn stably without transition of burning to detonation. If, however, a secondary explosive is porous or liquid, then in certain conditions with an increase of pressure the possibility appears of additional acceleration of burning due to an increase of its effective surface. At the expense of this accelerating, burning can become gas-dynamically unstable. In order to ensure maximum stability of burning, it is necessary to remove both possibilities of acceleration of burning, caused by the liquid aggregate state and caused by porosity.

A graphic illustration of these regularities is the obtaining of nitroglycerine powder from nitroglycerine and nitrocellulose. Both

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*If a particle during formation of a suspension was sufficiently heated, then later on their ignition reaction will go not only in form of burning on the surface of the particles, but also in their volume; with sufficient thickness of the reacting layer of the particles this can lead to thermal appearance of an explosion in it.

of these substances, which are by themselves typical secondary explosives, in combination give a typical powder, burning stably and very difficult to detonate. Each of these substances separately possesses the structure, which determines the possibility of development of one of the above considered mechanisms of the acceleration of burning.

Nitrocellulose is a solid matter, but in usual conditions has significant porosity, which determines during burning under increasing pressure the acceleration of the process of penetration of gases in pores. Nitroglycerine — a nonporous liquid substance — gives acceleration of burning due to the instability of the surface of burning liquid (Landau effect). In nitroglycerine powder (as well as in all contemporary powders of colloidal type), nonporous and nonliquid, both the above-indicated mechanism of acceleration of burnings are impossible and transition of burning to detonation does not have room at least up to pressures of several thousand atmospheres.

Thus, secondary explosives with use of them as powders do not have to be liquid or porous. However, not any nonporous substance with a small burning rate* which is a secondary explosive, constitutes a powder. During burning under rapidly increasing pressure, for instance in a closed space, stable burning is possible only in the case when under the appearance of a sharp rise of pressure, and also the temperature does not disturb the continuity of the substance.

Crystal explosives, differing by a small mechanical durability, can during the shown conditions of burning be destroyed. Destruction of solid structure leads to an increase of the surface of burning;

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*More exactly, with small acceleration of burning with pressure.

therefore explosives, consisting of non-durable particles, can give transition of burning to detonation. In order to avoid, when this is necessary, the possibility of such a transition, secondary explosives with the help of high polymers shift completely or partially into an amorphous state, in which they obtain great mechanical durability, but mainly, lose the ability to be split during the influence of rapid increasing pressure and sharp temperature gradients and preserve during burning as under a constant, as well as under an increasing pressure the initial form of their particles. In such a state secondary explosives are powders.

The preservation by particles of a powder of its form during burning allows on the basis of the same composition to prepare charges with a different duration of burning. If one were to make particles of powder thin, then they will burn fast. Charges from such powder will be useful for a weapon, which has a short barrel (pistol) or a barrel, calculated on small pressures (shot gun, mortar). Charges from powder with particles of great thickness will be able at the same pressure to burn for a correspondingly larger time and will be useful for a weapon with a long barrel. Along with this, by giving particles of powder a different form, it is possible to provide different laws of change of their surface in the process of burning and consequently also the speed of gassing in pores. Thus, the surface of particles having the form of a sphere or cube rapidly decreases by means of combustion; in the case of thin plates this decrease of the surface occurs much slower, with tapes or tubes, especially long — even still slower, and during burning of multichannel tubes the surface not only does not decrease, but even grows.*

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*If by measure of combustion the total surface of the particle of the powder decreases, then such a form of particles are called degressive. Such forms of powder grains, at which in the process of burning the surface is increased are called progressive.

All of this makes it possible to ensure the most expedient from the point of view of ballistics, change of pressure during a shot. Use of particles of relatively fragile or liquid secondary explosives, even those, which at high pressures burn without transition to detonation, does not make it possible to regulate gas forming by the simple means which contemporary smokeless powders do this.

§ 8. About the Practical Value of the Dependence of Speed of Burning of Powders on Pressure and Temperature

Strong dependence of the burning rate of powder on pressure is undesirable. Such dependence leads to degressiveness of the burning of the powder charge, increasing during the shot in relation of the maximum pressure to the average. It is desirable that the burning rate of the powder as less as possible depends on the initial temperature. If this dependence is great, then the relation of maximum pressures during firing in summer and winter time is increased.

The dependence of the burning rate on pressure and temperature during use of a powder charge in a jet engine shows especially strong. If the burning rate is directly proportional to the pressure, then such a powder, in general, cannot be used in a jet engine. This conclusion ensues fron an equation of the balance of gas forming at the expense of burning the powder charge and draining of gas through the nozzle. The weight of quantity q_1 of gases, forming per unit of time, constitutes

$$q_1 = u_m S, \qquad (4.31)$$

where u_m – mass burning rate of powder;

S – surface of powder charge.

The expenditure of gases q_2 through the nozzle per unit of time constitutes

$$q_2 = A\sigma p, \tag{4.32}$$

where A — coefficient of expenditure;

σ — minimum section of nozzle;

p — pressure in combustion chamber.

The dependence of the burning rate on the pressure and initial temperature of powder may be expressed by the general formula

$$u_n = \frac{Bp^\nu}{A_1 - B_1T_0}.$$

Placing this formula in the expression (4.31) and equating incoming and exiting of gases, obtain

$$\frac{Bp^\nu S}{A_1 - B_1T_0} = Ap\sigma,$$

whence

$$p = \left(\frac{BS}{A\sigma(A_1 - B_1T_0)}\right)^{\frac{1}{1-\nu}}. \tag{4.33}$$

From the expression (4.33) it is clear that the character of the dependence of the magnitude of equilibrium pressure on parameters of loading and the engine to a strong degree is determined by the magnitude of ν. If $\nu \geq 1$, then equilibrium between incoming gas and exiting gas in general, is impossible. With $\nu < 1$ this equilibrium is stable, besides the nearer ν is to one, the stronger the equilibrium pressure depends on parameters of the load and as the initial temperature.

A change of equilibrium pressure with a change of initial temperature of the powder is determined not only by the dependence of the burning rate on the temperature, bur also by its dependence on the pressure. Really, from the expression (4.33) it follows that

$$\frac{dp}{dT_0}\frac{1}{p} = \frac{1}{1-\nu}\frac{B_1}{A_1 - B_1T_0}, \tag{4.33a}$$

i.e., the relative change of equilibrium pressure with a change of initial temperature of the powder is defined as the influence of the temperature on the burning rate (through the second factor), as well as the dependence of the burning rate on pressure (through the first factor).

Therefore, if we have two powders, the burning rate of which increases an identical number of times during a given change of temperature, then the pressure will increase unequally, if the magnitude of ν for these powders is different. The less ν is, the less the equilibrium pressure increases with an increase of temperature. If the dependence of the pressure on the parameters of the charge and temperature is great, then this forces a combustion chamber with large reserve of durability to be made, i.e., to charge it, which, as is known without explanation, is undesirable.

Contemporary nitroglycerine powders are characterized by comparatively large values of ν: about 0.7. Therefore, for charges from these powders, the exponent in the expression (4.33) is sufficiently large; at $\nu = 0.67$ it is equal to three, with $\nu = 0.75$ – four.

The dependence of the burning rate on the temperature is also significant. With an increase of the temperature from -18 to +60° the burning rate increases 1.3-1.5 times.

The introduction of catalytical additions in a composition of powders manages to affect the dependence of speed of their burning on the pressure in such a way that at operating pressures, characteristic for rocket chambers, the burning rate slowly increases with the pressure (Fig. 4.34).

Catalytical additions also weaken the dependence of the burning rate on the temperature.

The burning rate of mixture powders, consisting of solid oxidizers (oxygen containing salts, for instance, ammonium perchlorate ammonia) and a fuel (synthetic rubber, resin, and so forth), as a rule, more weakly depends on pressure and temperature. In this respect, mixture powders are preferred as fuel for rockets over nitroglycerine powders.

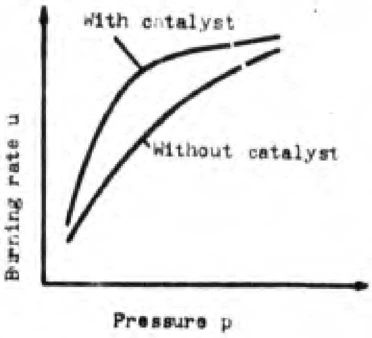
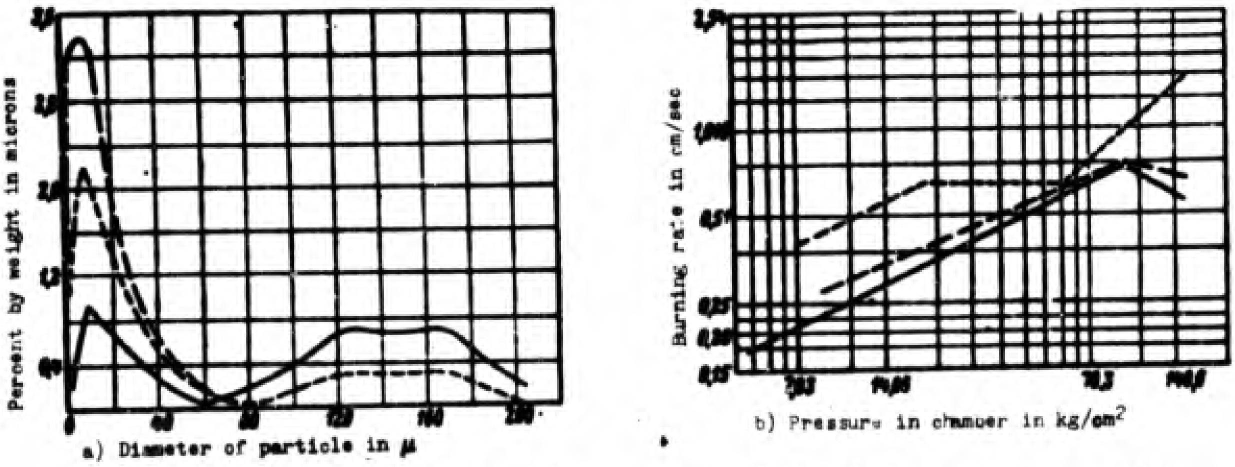


Fig. 4.34. The influence of catalysts on the dependence on pressure of the burning rate of nitroglycerine powder in a region of moderately high pressures.

It is necessary to add that ballistic, physical and technological properties of mixture rocket powders strongly depend on the dimensions of particles of the oxidizer and distribution of them by dimensions. By changing these characteristics, it is possible essentially to change not only the burning rate, but also the character of its dependence on pressure, as illustrated in Fig. 4.35, showing the dependence of the burning rate on pressure of a number of samples of a mixture powder of the same chemical composition, but with different dimensions of particles of the oxidizer.

Some of the mixture powders further have the advantage that they are able to burn stably and with full energy release at lower pressures than a powder of the ballistite type. Thanks to this, it is possible to decrease the thickness of walls and consequently also the weight of the rocket chamber and at the expense of this to increase either the weight of the warhead of the missile, or the distance of its flight.

A rocket charge usually consists of several powder tubes or rods. Gases forming during burning move along the burning surface with a speed, which increases by measure of the approximation to the nozzle. If this speed is great, then the flow of gases increases the burning rate of the powder. The probable cause of the increase of the burning rate is the increase of heat transfer from the moving gas to the surface of the powder. In the beginning of burning, when the area of the section of the chamber free from powder is small, the speed of the gases the biggest. If it exceeds a certain limit then gas forming is increased so much that pressure in the beginning of burning strongly increases as compared with its equilibrium value. This already by itself is not desirable, but, furthermore, it frequently leads to nonuniform burning with periodic rises and drops of pressure and the formation of products of incomplete chemical transformation, in particular, nitrogen oxides. In order to avoid these disturbances of normal conditions of burning, it is necessary to limit the relation of the beginning surface of forming to the free section of the chamber. This is attained either by use of powder tubes with a channel of sufficiently large diameter, or by partial armoring of the surface of charge, or by attaching a moderately progressive form to the charge.



a) Diameter of particle in μ

b) Pressure in chamber in kg/cm^2

Fig. 4.35. Dependences of the burning rate of a mixture powder on the pressure at different dimensions of particles of oxidizers. a) content (in percent by weight) of particles of different dimensions in the oxidizer, b) dependence of burning rate on pressure for samples of powder, prepared on an oxidizer of various degree of crushing.

During burning in the rocket chamber in known conditions sudden sharp and brief increases of pressure were observed. Experiments by interruption of burning showed that one of the causes of the appearance of peaks of pressure is the formation of burnt places on the powder cartridge. The causes of formation of burnt places have not been exactly determined. American researchers connect this phenomenon with the effect of radiation of powder gases on the burning of powder and, in order to prevent formation of burnt places, they introduce additions into the composition of powder, coloring it in a black color (soot, nigrosine, and so forth).

§ 9. Detonation of Condensed Explosive Substances

In practical conditions detonation of initial explosives is excited by means of igniting them or sharply striking them; with this the burning appearing rapidly passes to detonation. Detonation of secondary explosives is usually excited by a percussion-detonator; in case of low-sensitivity explosives a multistage initiation is used: a percussion-detonator in combination with an intermediate detonator — a small charge more sensitive to detonation of the explosive.

In theory of explosives and in the practice of their use the velocity of detonation has an exclusively important meaning.

On the one hand, the speed of propagation is a most important characteristic of the process of detonation, determining a number of properties of the latter; the study of the speed of detonation and its dependence on conditions of explosion and properties of the charge makes it possible to make most important conclusions about the mechanism of the process, about equation of the state of products of the explosion and so forth. On the other hand, speed in distinction to certain other characteristics of detonation is of such magnitude, which can, comparatively simply, be measured with great accuracy and reliability.

Table 4.13. Speed of Detonation of Certain Explosives (According to Cook)

Explosives	Density ρ_0 in g/cm^3	Speed of detonation D_{ρ_0} in m/sec	Coefficient M m/sec: g/cm^3
Trotyl	1,0	5010	3225
Tetranitrate	1,0	5550	3950
Pentolit 50/50 (tentranitrate-trotyl)	1,0	5480	3100
Hexogene	1,0	6080	3590
Tetryl	1,0	5600	3225
Tetritol 65/35 (tetryl-trotyl)	1,6	7300	3400
Picric acid	1,0	5255	3045
Ethylenedinitramine	1,0	5910	3275
Ammonium picrate	1,0	4990	3435
Nitroguanidine	1,0	5460	4015
Lead azide	4,0	5100	560
Mercury fulminate	4,0	5050	890
Ammatol 50/50	1,0	5100	4150
Sodatol 50/50 ($NaNO_3$-TNT)	1,0	4100	2580
Dyne (dinitrate dioxyethylnitramine $C_4H_8N_4O_8$)	1,0	5050	2930
Neno (dinitrate dioxyethyldinitroxamide $C_6H_8O_{12}N_6$)	1,0	5630	3660
Nitroglycerine liquid	1,50	7700	—
Nitroglycerine-dinitrotoluene 60/40	1,50	7000	—

For various explosives the speed of detonation lies from 1000 to 9000 m/sec. The values of the speed of detonation for a number of explosives are given in Table 4.13.

In the third column of Table 4.13 are shown the values of the speed of detonation with the density of charge, given in the second column. For solid organic explosives, consisting of C, H, N, and O, with densities from approximately 0.5 g/cm^3 to maximum the speed of detonation is linearly combined with the density,

$$D_{\rho_1} = D_{\rho_0} + M(\rho_1 - \rho_0). \tag{4.34}$$

Using the value of the coefficient of M given in Table 4.13, it is possible by equation (4.34) to calculate the speed of detonation at densities different from the density shown in the second column.

Martin and Yallop determined simple semi-empirical relationships, connecting the speed of detonation of organic explosives in a liquid, cast or pressed state with their oxygen balance and density of charge. The experiment showed that at a given density the speed of detonation or organic explosives, having a negative oxygen balance, linearly depends on the speed taking a maximum value when the oxygen balance becomes equal to zero. This is not surprising, since the energy, separated during detonation, and the composition of products essentially depend on the oxygen balance in these explosives. However, the usual expression for the oxygen balance does not consider the circumstance that atoms of oxygen in a molecule of the explosive in a nitro group, in a CO-group and others are powerfully unequally valued; considering this, the authors express the oxygen balance Ω formula

$$\Omega=\frac{(z-2x-y/2)100}{n}\pm\frac{100w}{n}, \tag{4.35}$$

where z, x, y are the number of atoms of oxygen, carbon, and hydrogen in a molecule; n is the total number of atoms in a molecule; they calculate the w correction, summarizing a number of atoms of oxygen with different coefficients; for an atom of oxygen, connecting a nitro group with carbon — the coefficient is equal to 1; for the C = = O-group — the coefficient is 1.8 and for the C-OH-group — the coefficient is 2.2. The sign of correction corresponds to the sign of the first component. Knowing the oxygen balance, it is possible with an error, not exceeding 2%, to express the speed of detonation with $\rho = 1.6$ g/cm^3 by the relationship

$$D=8678+33{,}74\Omega. \tag{4.36}$$

For calculation of the dependence of speed of detonation on the density the relationship is obtained:

$$D=2500+13{,}25\Omega+3793\rho+12{,}81\Omega\rho. \tag{4.37}$$

Even better conformity of calculating and experimental data is obtained in the case when the heat of the formation of the explosive is considered. Then

$$D=2880+11{,}97\Omega_1-0{,}706H+3764\rho+13{,}67\rho\Omega_1+0{,}108\rho H. \tag{4.38}$$

where H is the heat of formation of the explosive in kilocalorie/kg; the oxygen balance Ω_1 is calculated, taking in this case somewhat different values of coefficients for numbers of atoms of oxygen than indicated above, and namely: for the nitro group — 0, for C-O-N-0.5, and for C = 0, and C-O-H-groups — 1. If the heat of formation of H is unknown, then it can be calculated by the heat of combustion and structural characteristics of the molecule of the compound (see p. 608).

The speed of detonation of a given explosive during fulfillment of known conditions is its constant. For a charge of usual cylindrical form, the detonation of which is excited from one of the faces, such conditions are maximum density and diameter, exceeding a certain definite magnitude, a so-called limiting diameter d_{lim} (Fig. 4.36).

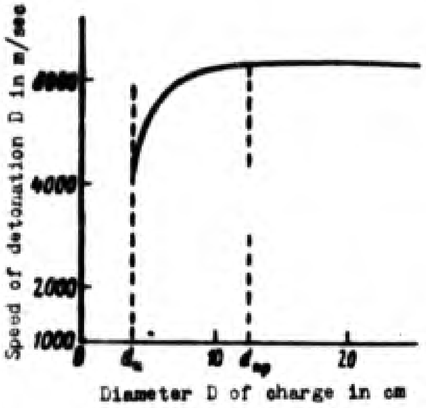


Fig. 4.36. The dependence of the possibility and speed of detonation of an explosive (ammatol 50:50 with a density of 1.53 g/cm^3) on the diameter of the charge. d_c — critical diameter, d_{lim} — limiting diameter. [к = c = critical, пр = = lim = limiting]

If one were to take a diameter of charge less limiting, then the speed of detonation would also be less. However, below a certain minimum, the so-called critical diameter d_c, the detonation will not be spread stably by charges. With diameters below the limiting the speed of detonation depends on the presence and characteristics of the shell of the charge, on the dimensions of particles of the explosive (especially in the case of mixtures) and on its physical structure. These factors also influence the magnitude of the critical diameter. Furthermore, the density of the charge also renders an influence on the speed of detonation and critical diameter.

Below we will consider basic results of experimental research on the influence of different factors on the possibility of detonation and the speed of its propagation for various explosives.

1. The Critical Diameter of the Charge and Its Dependence on Different Factors

It is known that various substances, being explosive, differ by their ability to explode. The standard measure of this ability (explosiveness) is, as was established by Yu. B. Khariton, the critical diameter of the charge: the more explosiveness, the correspondingly less critical diameter.

The magnitude of the critical diameter characterizes the speed of chemical transformation during explosion. This speed, however, is determined not only by activation energy or by the speed constant, as is for simple chemical reactions. Chemical transformation during explosion of a condensed explosive has a complicated character and usually flows in the form of burning of a great number of separate particles. These can be initial particles of the explosive or particles, which were formed as a result of micro-heterogeneous appearance and the development of the reaction in it. The temperature and pressure, attained during explosion also essentially affect the course of transformation and its speed. For that reason, speed increase depends on its heat effect, and also on the presence and resistance of the shell, which hampers expansion of gaseous products of the reactions. On the strength of these causes explosiveness is determined not only by chemical-kinetic and thermal characteristics of the explosive, but also by its physico-mechanical properties, and also by external conditions, from which depend the formation and dimensions of the burning particles. The integral expression all these factors is obtained in the magnitude of the critical diameter. It is clear that the critical diameter is not constant for a given explosive regardless of conditions of its explosion. During a change of these conditions the critical diameter can be changed within wide limits.

The critical diameter is practically determined by the following form: cylindrical charges of the given explosive of a various diameter is detonated and each time it is determined whether the detonation went to the end of the charge or dampened, which can establish by means of photoregistration or by the state of the lining, on which the charge was located charge. The least diameter of the charge, at which stable detonation (without damping) is still possible is also considered critical.

During experiments it is necessary to watch, so that damping of detonation is combined namely with achievement of critical sizes, with incapability of the system to propagate detonation, and not with weakness of the initiator. Standard percussion-detonator No. 8 can ensure detonation of powered explosives only in the case, if $d_c <$ $< 15\text{-}20$ mm, and cast explosives, if $d_c < 5\text{-}10$ mm; otherwise an intermediate detonator is necessary.

We will underline once again that the critical diameter depends not only on chemcial properties of the explosive, but also on its physical state and conditions of the explosion (aggregate state of the explosive, its density, dimension of particles, character of shell, and so forth).

In Table 4.14 are given tentative data about critical diameters of certain explosives during possibly similar conditions of explosion and possibly close physical state (powdered explosives with identical density 0.9-1.0 g/cm^3, close dimensions of crystals 0.05-0.2 mm, and identical character of the shell-glass tube), i.e., under conditions, when the distinction in the magnitude of critical diameters is determined in the largest degree by chemical factors.

Table 4.14. Critical Diameter of Several Powdered Explosives

Explosives	Critical diameter d_c mm
Lead azide	0.01—0.02
Tetranitrate	1.0—1.5
Hexogene	1.0—1.5
Lead picrate	2—3
Picric acid	6
Trotyl	8—10
Ammonite No. 6 (21% trotyl and 79% ammonium nitrate)	10—12
Mixture 20% aluminum and 80% ammonium nitrate	12
Mixture 10% trotyl and 90% ammonium nitrate	15
Ammonium nitrate	100

From Table 4.14 it is clear that with close physical conditions of the value of critical diameters (the most important characteristic of explosiveness) are distinguished very strongly: for extreme cases (lead azide and ammonium nitrate) — five-ten thousand times.

A comparison of critical diameters for different chemically monotypic explosives shows that the less this diameter is, the greater the heat of explosion. However, exceptions to this rule are frequently observed. During a comparison of explosives, sharply differing in chemical structure, like lead azide and trotyl, the simple connection between the heat of the explosion and critical diameter is not observed.

In Table 4.15 are given values of the critical diameters of certain liquid explosives during explosion in glass tubes or thin-walled capillaries.

It is interesting that the critical diameter of liquid explosives, as established on the example of trotyl, nitromethane, and nitroglycerine, is significantly increased with lowering of the temperature.

We will turn now to data about the influence of individual physical parameters and conditions of explosion on the magnitude of the critical diameter.

Table 4.15. Critical Diameter of Several Liquid Explosives

Explosives or mixture	Critical diameter d_c in mm
Tetranitromethane/benzene (87.5/12.5)	<0.1
Nitric acid/nitrobenzene (72/28)	0.5
Nitroglycerine	2.0
70% nitric acid/methyl alcohol (70/30)	>10
Trotyl liquid at 81°C	62
Trotyl liquid at 240°C	6.0

The dependence of the critical diameter on the <u>physical state of the substance</u> may be illustrated by data of Apin and Bobolev on an example of trotyl (Table 4.16), obtained during the explosion of charges in glass tubes with an internal diameter of 10 mm. The poured trotyl was obtained by slow thickening of melt and consisted of attached large crystals.

Table 4.16. The Ability of Trotyl in a Different Physical State to Detonation

Physical state of trotyl	Density in g/cm^3	Temperature in °C	Initiator	Results of experiment
Liquid	1.46	+100	20 g of pressed tetranitrate	Rejection
Pressed powder	1.46	-180	Percussion-detonator No. 8	Full detonation, D = 6600 m/sec
Poured in large-crystals combined state	1.64	+20	20 g pressed tetranitrate	Rejection

Whereas trotyl in the form of pressed powder detonates even at -180° from a comparatively weak initiator (percussion-detonator No. 8), liquid and poured trotyl cannot detonate in these conditions. In other words, the critical diameter for a pressed powder is less than 10 mm, and for poured or liquid trotyl – significantly higher. Further experiments showed that poured trotyl can detonate with a diameter of the charge of not less than 32 mm, powdery fine-crystalline trotyl of the same density detonates, when the diameter of the charge constitutes all of 2.1 mm. Thus, the critical diameter of poured trotyl is 15 times more than powdered.

The influence of the physical structure on the ability to detonation is the especially graphic example of nitroglycerine powder. Both its components (nitroglycerine and nitrocellulose) by themselves detonate very easily – with small diameters of the charge. In the powder, apparently, because of its extremely great viscosity and absence of pores the appearance and propagation of detonation is very hampered (see p. 270), and it detonates only with a much larger diameter charge.

For individual powdered explosives (trotyl, picric acid, tetranitrate, hexogene, po assium, and lead picrates) and their mixtures the critical diameter, according to Bobolev, depends on the density and dimensions of particles in the following form: the greater the density of the explosive and less the dimensions of its particles, the greater the detonational ability and less critical diameter. Figure 4.37 shows the dependence of critical diameter of a charge on the density for macrocrystalline and fine-crystalline trotyl. The influence of the dimensions of particles on the critical diameter for various explosives is shown in Table 4.17 (experiments in glass tubes).

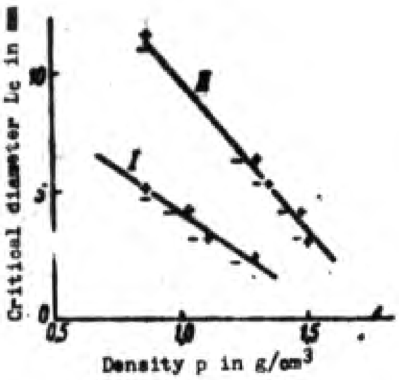


Fig. 4.37. Dependence of critical diameter of a charge of trotyl with various dimensions of particles on the density. I – particles with dimensions of 0.01-0.05 mm, II – the same 0.07-0.2 mm. < + > – detonation, < - > – rejection.

An analogous influence of the density on critical diameter was also observed for a gelatinous explosive – nitrogelatine. Nitrogelatine, with no air bubbles, having a density of 1.59 g/cm^3, detonated even in charge with a diameter of 3 mm, whereas with a density of 1.48 g/cm^3 detonation took place only in charges with a diameter of not less than 7 mm, and with a diameter of 5 mm rejections were always obtained.

For ammonium nitrate mixtures on the basis of nonexplosive fuel (peat) the influence of dimensions of particles of components, the density and shell was studied by Belyayev. He showed that the thinner the crushing of components of peat diamine (12% peat, 88% ammonium nitrate), the greater its detonational ability, consequently, in this respect the mixture is similar to the individual explosive. With respect to the influence of density, the picture obtained is reverse. The higher the density, the greater the critical diameter of the studied mixtures (Table 4.18).

From data in Table 4.18 it is clear that a charge of diamine of thin crushing detonates with a density, equal to 1 g/cm^3, even with a diameter of 15 mm; in order to obtain detonation of a diamine of average crushing with the same density, a diameter of 35-40 mm is required. If density of the diamine of thin crushing increases from 1.00 to 1.22 g/cm^3, then the critical diameter increases from 15 to 40 mm, i.e., almost by three times.

Table 4.17. The Influence of Dimensions of Particles on the Critical Diameter of a Charge

Explosives	Dimensions of particles in mm	Critical diameter d_c in mm *	Density ρ g/cm^3
Trotyl	0,01—0,05 0,07—0,2	4,5—5,4 10,5—11,2	0,85
Picric acid	0,01—0,05 0,05—0,07 0,1—0,75	2,08—2,28 3,6—3,7 8,9—9,25	0,8 0,7 0,95
Potassium picrate	0,04—0,15	5,5—6,0	0,75
Lead picrate	0,01—0,05	1,45—1,53	0,75
Tetranitrate	0,025—0,1 0,15—0,25	0,70—0,86 2,1—2,2	1,0
Hexogene	0,025—0,15	1,0—1,15	1,0

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*The first number signifies the diameter, at which detonation no longer spread, the second – at which propagation of detonation still occurred.

Table 4.18. Dependence of the Critical Diameter of Peat Diamine on the Degree of Dispersiveness of Components and on the Density

Density of diamine from components of various crushing in g/cm^3			Critical diameter d_c in mm
thin	average	coarse	
0,91	—	—	11
1,00	0,71	—	15
1,06	0,80	—	20
1,12	0,87	—	25
1,16	0,93	—	30
1,19	0,98	0,70	35
1,22	1,03	0,77	40
—	1,10	0,85	50
—	1,17	—	62,5

The distinction between separate explosives and mixed of the considered type* can be explained by the following. With an increase of density the dimensions of gas pockets in the powder and its gas-penetrability are decreased. As a result of this ignition of particles of the explosive should be hampered as in the case, if it occurs due to compression and heating up of gas pockets, as well as in the case when it evokes hot gases, penetrating in pores between the particles. The inflammability of particles of the mixtures, consisting of non-explosive or weak-explosive components, or weak individual explosives, is relatively small and ignition of them with large densities may be hampered so much that in a charge of small diameter detonation becomes impossible. Along with this, in the case of mixtures with too large pressure, appearing during detonation of an explosive of large density, development of the reaction may be delayed, which includes not only reaction of separate particles, as in individual explosives, but also mixing of products of the reaction of particles of different components. The basic energy content separates after mixing – during the interaction of products of the reaction of separate components.

Experiments on the influence of the shell show that its presence facilitates propagation of detonation, lowering the critical diameter for mixtures, as well as for separate explosives.

According to Belyayev the presence of the shell first is approximately equivalent to increasing the diameter of the charge and the question about the influence of a massive shell on the stability of detonation may concern the question of the influence of the diameter

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*According to data of I. F. Blinov, similar to the considered mixtures are also weak separate explosives, for instance a dinitrocompound of aromatic hydrocarbons.

of the charge. The action of shell is determined first of all by its mass, and not durability. Correspondingly lead shells are more effective than iron. Use of a thick shell can very strongly lower the critical diameter. Even such a low-sensitive to detonation explosive, as ammonium nitrate detonates with diameter of 7 mm in the case when it is placed in a steel shell with a thickness of 20 mm.

2. Dependence of the Speed of Detonation on the Diameter of Charge, Dimensions of Explosive, and Character of the Shell

With an increase of the diameter of the charge above the critical the speed of detonation increases, asymptotically nearing its own limit value. For solid explosives the relative increase of speed of detonation during transition from critical diameter to limiting is small ($D_{cr} \approx 0.9$ to $0.95D_{max}$), for powdered explosives of small density it is more ($D_{cr} \approx 0.4$ to $0.5D_{max}$). With this the relative velocity of detonation (D/D_{max}) is approximately determined by the relation of diameters of the charges d/d_{lim}. In accordance with this, the speed of detonation is fast — during an insignificant increase of the diameter — increases for explosives having small critical diameter. Thus, nitrogelatine of great density, not detonating in a charge with a diameter of 2 mm, in charge with a diameter of 3 mm detonated with a speed of 7600 m/sec; with diameters of 4 and 5 mm the speed was the same, 7800 m/sec. According to Bobolev, in the case of hexogene (Fig. 4.38) already with a diameter of almost 2 mm constant maximum (for the given density nearly 1.0 g/cm^3) speed of detonation is practically attained. For trotyl the growth of speed of detonation occurs slower, where dimensions of the crystals (Fig. 4.39) play a role. The speed of detonation in the case of a fine-crystalline powder (0.01 - 0.05 mm) more quickly nears the limiting value than

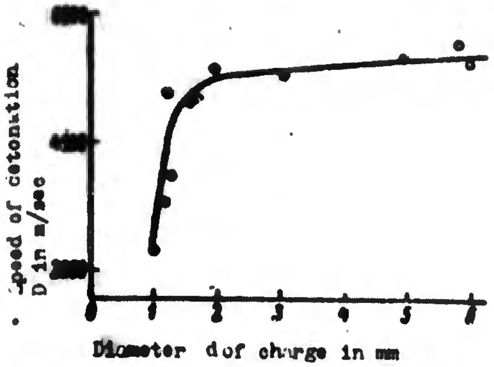

Fig. 4.38. Dependence of the speed of detonation of hexogene of moderate density on the diameter of charge.

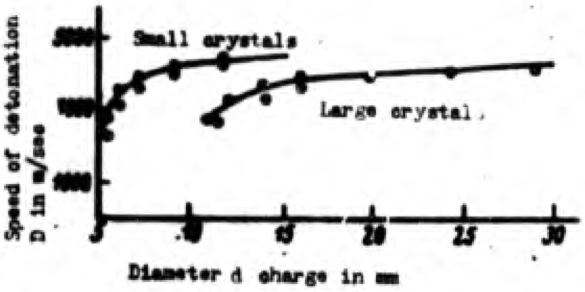

Fig. 4.39. Dependence of the speed of detonation of trotyl ($\rho = 0.85$ g/cm^3) on the diameter of charge.

in the case of macrocrystalline (0.07 - 0.2 mm), when it still continues to grow to the largest tested diameter — 30 mm.

From what has been said, it follows that with diameters of a charge less limiting the speed of detonation depends on the dimensions of the particles, the speed may be noticeably larger for a small crystal substance. With large diameters of charge the speed of detonation, apparently, is identical for powders with various dimensions of particles.

In case of such difficult detonating explosives, as ammonium nitrate, especially in the granule form, the speed of detonation may be far from the maximum even with significant diameters of the charge, 300 - 320 mm.

The above noted the positive influence of the shell on the possibility of detonation. The shell also renders an analogous influence on the speed of detonation (Table 4.19). As can be seen, with diameters of a charge less limiting the presence of shells of materials of great density and durability noticeably increases the speed of detonation. This influence of the shell is especially significant (for separate explosives) with average densities; with large densities it is absent; with small — appears much weaker.

If the diameter of a charge is more limiting, then the presence and character of the shell do not change the speed of detonation, as this is shown in Table 4.20.

Table 4.19. Influence of the Shell on the Speed of Detonation of Explosives

Explosives	Material of shell	Diameter of charge in mm / Thickness of walls of shell in mm	Density in g/cm^3	Speed of detonation D m/sec
Trotyl	Glass	25/1	0,250	2363
	Steel	27/4		2478
	Glass	16/0,8	0,832	3308
	Copper	15/1		4100
Tetryl	Paper	5/0,08	0,240	2605
	Glass	5/1		2900
Tetranitrate	Glass	16/0,8	0,300	3419
	Copper	15/1		3548
Methylnitrate	Glass	3/1	—	1900
		3/2	—	2200
		3/4,5	—	2400

Table 4.20. Influence of the Shell on the Speed of Detonation of Explosives

Explosives	Diameter of charge in mm / Thickness of walls of shell in mm	Speed of detonation D m/sec
Cast trotyl	Steel	
	21/3	6555—6700
	29/10	6700
	75/14.5	6685
	100/25	6690
	220/50	6675
	300/80	6710
Tetryl (ρ = 1.69 g/cm^3)	Copper	
	7/0.23	7022
	21.2/0	7025

3. Dependence of the Speed of Detonation on the Density of the Charge, Initial Impulse, Impurities, Temperature, and Pressure

An increase of density increases the speed of detonation of individual powerful explosives. For tetranitrate and picric acid this influence is illustrated by the curves of Fig. 4.40, on which along the axis of the abscissas is plotted the "relative density" ρ/d, i.e., the relation of the density of the charge to the specific gravity of the explosive.

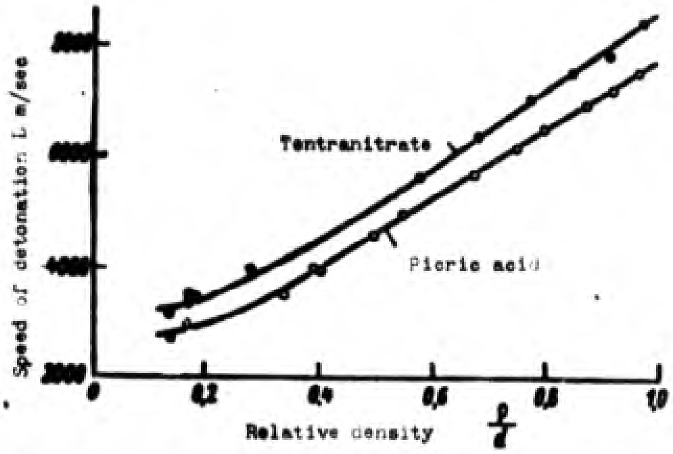

Fig. 4.40. Dependence of the speed of detonation of individual powerful explosives on the density.

For mixtures, the components of which by themselves do not explode or have little sensitivity to detonation explosives, with an increase of density the speed of detonation increases in the region of moderate densities, passes through the maximum and then drops.

In Fig. 4.41 are given the results of experiments of Dotrish on the definition of the speed of detonation of cheddite* with different densities.

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*Cheddite is an explosive mixture on the basis of potassium chlorate.

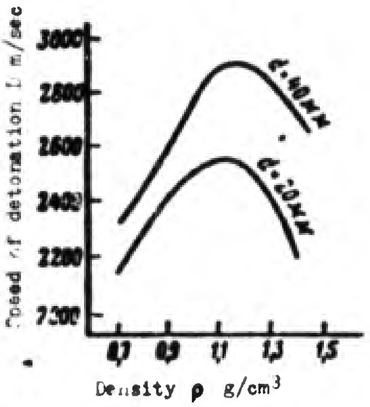

Fig. 4.41. Dependence of the speed of detonation of cheddite on the density with different diameters of the charge d.

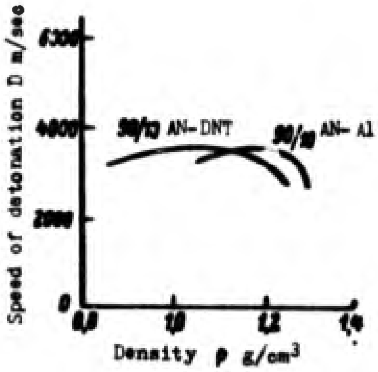

Fig. 4.42. Dependence of the speed of detonation of mixtures of ammonium nitrate (90%) with dinitrotoluene (10%) or aluminum (10%) on the density with a small (10 cm) diameter of charge.

Figure 4.42 shows according to Cook, the dependence of the speed of detonation of mixtures of ammonium nitrate with dinitrotoluene and with aluminum on the density. Such dependence is characteristic, apparently, not only for mixtures of the shown type, but, according to Blinov, also for separate explosives, differing by small detonational ability, as ammonium nitrate, dinitrotoluene, dinitrophenol, and so forth. The position of maximum of speed depends, however, on the diameter of the charge; the greater this diameter, the higher density at which the speed of detonation passes through the maximum. A shell renders an analogous influence. Therefore, using sufficiently large diameter and thick shells, it is possible to transfer the position of maximum to a density, equal to the specific gravity of the explosive. In these conditions for mixtures of the type of curve D = f(ρ) will correspond to that observed for powerful separate explosives.

From what has been said it follows that an increase of the density in a definite interval of it in the case of mixtures with small diameters of charge decreases not only the possibility, but also the speed of detonation.

Imagine that we took, for instance, trotyl, the detonation of which is facilitated with an increase of density in all respects of its possible interval, and began to mix it with ammonium nitrate. It is obvious that with small diameters of charges we have to observe with any content of nitrate a transition from the type of influence of density, characteristic for trotyl, to a type, characteristic for mixtures. Bobolev, studying ammatol 50:50, established a very interesting fact: for the same mixture it is possible to observe two types of dependence — in charges of moderate diameter detonation is possible with small and with large densities, but does not spread with intermediate. In the region of small densities the critical diameter increases with an increase of the density, as this should be for a mixture, and in region of large densities the diameter decreases, as this is typical for separate explosives (Fig. 4.43).

The influence of the force of initial impulse on the speed of detonation was noted by Dotrish for picric acid. The explosive was detonated with a density of 1.73 - 1.74 g/cm^3 in paper ammunition with a diameter of 20 mm. With the initiator in the form of 0.5 g of mercury fulminate and 15 g of dynamite the speed of detonation constituted 7280 m/sec, and with an increase of the charge of dynamite to 80 g — 7650 m/sec. However, in this and analogous cases there is talk not about the increase of stationary speed of detonation, as such, but about the reduction with a strong impulse section of acceleration. In conditions of the given experiments, when the average speed of detonation on a comparatively short section near the

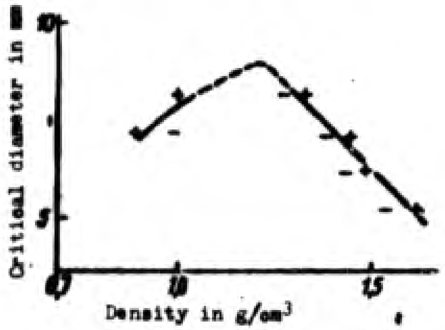

Fig. 4.43. Dependence of critical diameter of ammatol 50:50 on the density. < + > — detonation, < - > — rejection.

initiator was determined, the given circumstance conditioned an apparent increase of speed. An analogous phenomenon is observed in the case when the explosive with a small speed of detonation is initiated by a powerful initiator; then the initial section speed of detonation will appear higher than normal, but with distance will decrease, nearing it.

Another influence of the initial impulse on the speed of detonation is also difficult to allow, since its role leads only to excitation of the explosion, to further initialing for every subsequent layer serving as a preceding layer of the explosive.

An exception are those conditions, in which certain explosives can detonate with different speeds. This phenomenon long ago was revealed for nitroglycerine and dynamite, but later was established also for other liquid esters. It was observed also for powdered secondary explosives (trotyl, tetryl, picric acid, tetranitrate, and hexogene), although in this case the distinction in speeds of detonation is not so great, as for liquid explosives, and appears not so clear. Even initial explosives – mercury fulminate – in strongly pressed (pressure of pressing 4200 kg/cm^2) form is able to detonate with a diameter of charge of 4 mm with small speed, lying from 1200 to 1700 m/sec.

An essential factor, determining the appearance of small or great speed of detonation, is the force of the initial impulse. For nitroglycerine in glass tubes of different diameter during excitation of explosion by various initiators the speed of detonations given in Table 4.21 was obtained.

With an increase of the diameter of the tube from 6 to 12 mm, the small speed of detonation increases; with further increase of diameter strong oscillations of results are observed and the small

Table 4.21. Speed of Detonation of Nitroglycerine in Different Conditions

Diameter of charge mm	Speed of detonation D during initiation by percussion detonator m/sec			
	No. 2 mercury fulminate	No. 6 mercury fulminate	No. 8 mercury fulminate	No. 8 aziodo-tetryl
6	890; 950	810; 890; 1030	1350	8130*
12	2530	1940; 2090	1780	8700
18	2130	1970; 2030	1750	8250; 8390
25	2190	2020; 2030	—	8130
32	1760	1780; 2010	—	8140
38	—	1910	—	—

Note: The charge of percussion-detonator No. 2 constitutes 0.4; No. 6 – 1.0; and No. 8 – 2.0 g of mercury fulminate.

speed of detonation is not changed. In the case of using an azidotetryl detonator with all diameters from 6 to 30 mm detonation spreads with great speed, exceeding the small by approximately 4 times.

In long charges of nitrogelatine, especially with their large diameter, usually at a certain distance from the initiator the small speed of detonation by a jump passes to a large; if one uses an intermediate detonator, then always immediately a high speed is obtained. Detonations with great speed is also promoted according to Dempster by the introduction in dynamite of a small quantity of small (0.5-10 μ) particles of certain inert heavy ($\rho > 2.8$ g/cm^3) substances ($BaSO_4$, $BaCO_3$, SiC, talc, and others). Sensitizing action of impurities according to Avogadro is increased also with the hardness of the substance, which can to a known degree compensate for the influence of insufficiently high density.

For trotyl with corresponding conditions (dimensions of particles, density, diameter of charge, and others) with a small and constant

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*These speeds were defined according to method of Dotrish (see § 10); judging by data of the latest research, they are somewhat oversized.

speed of detonation it is possible to observe a significant length of charge. With a more powerful initiator in the same conditions high speed is obtained.

Thus, scaly trotyl* with a density of 1.0 g/cm^3 and a diameter of charge of 21 mm detonated with a speed at 1120 m/sec with initiation by azidotetryl percussion-detonator No. 6, with an intermediate detonator in the form of a tetryl cartridge by weight 12.5 g the speed constituted 3660 m/sec. For tetranitrate with a small diameter of charge Apin and Bobolev observed intermittent deceleration of detonation from 4100 to 2500 m/sec.

Impurities of inert substances in an explosive, in general, lower the speed of its detonation and ability for it. Thus, the speed of detonation of nitroglycerine is 7430 m/sec; the speed of detonation of a mixture of 75% nitroglycerine and 25% kieselguhr constitutes 6630 m/sec.

Certain inert impurities relatively weakly affect the ability of explosives to detonation. For instance, a mixture of nitroglycerine with sodium bicarbonate, containing a total of 10% nitroglycerine, turns out to be able to detonate. In general, the influence of solid inert impurities depends on the dimensions of their particles, which determine the specific surface of the impurity and correspondingly the speed of absorption by it of the energy of explosion. Apparently, the mutual distribution of explosive and inert components, and speed of detonation also play a role.

In certain cases, however, inert impurities increase the speed of detonation. Thus, according to Abel, moist pyroxylin detonates with

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*A fraction was used which passed through a sieve with 8 openings/cm and remaining on the sieve with 12 openings/cm.

a speed of 6100 m/sec instead of 5300 m/sec for dry pyroxylin. The speed of detonation of flegmatized paraffin of mercury fulminate is greater than for nonflegmatized. Such action of water and paraffin on pyroxylin and mercury fulminate is combined with a change of composition of products of the explosion.

The influence of temperature of the explosive on speed of detonation of a number of powdered explosives was studied, which detonated in thin-walled lead tubes with a diameter of 12.5 mm at temperatures of +25, -80, and -183°C (Table 4.22).

The results of experiments show that even very strong cooling does not render a definite influence on the speed of detonation. However, oscillation of speed at low temperatures is greater than at usual temperatures.

The absence of influence of temperature on the speed of detonation can be explained by the fact that the change of temperature was limited and was correspondingly insignificant as compared to the heat of the explosion to the change of heat contents of the explosive. With this, it should be considered that with a decrease of temperature the density of the explosive is increased and this can in a known measure compensate for the influence of lowering the heat and temperature of the explosion on the speed of detonation.

For certain poured explosives with a decrease of the initial temperature the speed of detonation increases somewhat, which undoubtedly, is combined with the increase of density. In the case of liquids, the density of which more strongly depends on the temperature than the density of solid explosives, the speed of detonation is noticeably increased with lowering of temperature. Thus, nitromethane at +60°C

Table 4.22. Dependence of the Speed of Detonation of Several Explosives on the Temperature

Explosives	Density in g/cm^3	Speed of detonation D in m/sec at temperature of		
		+25° C	−80° C	−183° C
Mercury fulminate	1,69	3330 3200 3260	3060 2960 3270	3150 3170 —
		Av. 3260	3100	3160
Picric acid	0,98	4750 5000 5150	4390 4600 4130	4750 4840 —
		Av 4970	4370	4800
Ammonium picrate	0,86	4110 4100 3850	4240 3960 3980	3920 4110 —
		Av 4020	4060	4020
Trotyl	0,90	4310 4460 4580	4800 4230 4260	4550 4570 4800
		Av 4450	4430	4640

detonated with a speed of 6100 m/sec; at -20°C the speed of detonation increased to 6400 m/sec. An increase of speed of detonation with a decrease of temperature is observed, according to Belyayev and Kurbangalina, also and for nitroglycerine.

Experiments on powered explosives, and also on gelatins, containing air effervescene, showed that their detonational ability and speed of detonation are essentially lowered with an increase of the pressure under which the explosive is. Thus, according to experiments of Bouden, in a film of powdered tetranitrate the detonation is spread, besides with small speed, if the pressure of the gas, under which the tetranitrate was, constituted one atm (tech.). At pressures higher than 30 atm (tech.) the speed of detonation is rapidly decreased, and at a pressure of 50 atm (tech.) and higher the propagation of detonation is discontinued soon after its beginning or it does not quite appear.

An analogous influence of the pressure on propagation of detonation was also noted for tetryl, trotyl, and nitroguanidine.

These observations can be explained by the fact that in conditions of the shown experiments during propagation of detonation compression of gas pockets in explosives played a large role; the higher the temperature obtainable with this compression, the less initial pressure of the gas.

§ 10. Methods of Determination of the Speed of Detonation of Explosive Substances

Let us consider briefly contemporary methods of determination of the speed of detonation. The majority of earlier used methods (chronographs of Mettegang, Boas, condensing chronographs, and so forth) required carrying out of tests on charges of significant length and, in spite of this, the experiments differed by a small accuracy of measurement. From these old methods we will consider only the method of detonating cord (the Dotrish method), which also possesses low accuracy, but is exclusively simple and therefore is applied also at the present.

1. The Dotrisha Method

The essence of method consists of that, the unknown speed of detonation of the charge is compared with the known speed of detonation of the detonating cord.

Figure 4.44 gives the diagram of the test. A section of detonating cord 2 of arbitrary length is packed in such a manner so that the ends of it touch the charge, but middle is on lead plate 3, as was shown in Fig. 4.44. If charge consists of a powdered explosive with a comparatively small speed of detonation, then the ends of cord must be put somewhat deeper in the explosive (both to an identical depth).

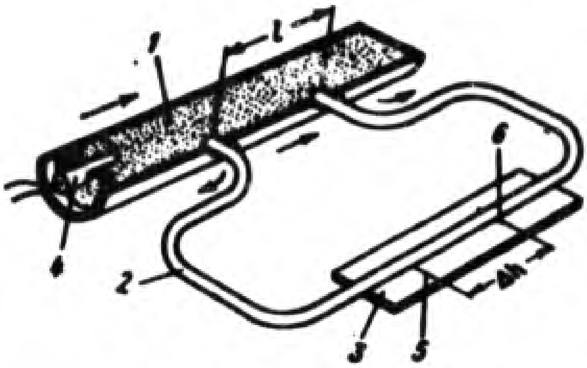

Fig. 4.44. Diagram of determination of the speed of detonation according to Dotrish. 1 — tested charge of explosive; 2 — section of detonating cord; 3 — lead plate; 4 — percussion-detonator; 5 — middle section of the cord; 6 — mark on plate after explosion.

The distance between the ends of the cord l is the base for determination of the speed of detonation and should be measured exactly. The detonation spreading along the charge evokes consecutive detonation of first the left, and then the right end of the cord. Thus, in cord will appear two detonational waves, moving toward each other. At a certain point of cord these waves will meet. During the collision of detonational waves the pressure will increase significantly (more than twice) and on lead plate, in a corresponding place, will be obtained a characteristic mark — deepening.* If detonation of the left and right ends of the cord is begun simultaneously, then collision of waves (and correspondingly the mark) will be obtained at point 5 exactly in the middle of the section of the cord. In reality in left end of cord detonation starts earlier than in the right, therefore the place of collision of the waves will shift to the right and will be at a point 6, where the mark will also be obtained. Quantity Δh designates the distance between the middle of the section of the cord and the place of collision of the waves. It is obvious that the propagation time of detonation by the left part of the cord t_1 to the moment of collision is equal to the time of propagation of detonation by charge t_{ch} on length l plus the propagation time of detonation by the right side of cord t_r to the place of collision,

---

*A mark is obtained more clearly, if the cord is raised above the plate by several millimeters.

$$t_{\text{л}}=t_{\text{зар}}+t_{\text{п}}.$$

[л = l = left; зар = ch = charge; п = r = right]

Quantity L designates the length of section of the cord, but D_c is the speed of its detonation.

Let us assume that D is the unknown speed of detonation of charge. Then

$$t_{\text{л}}=\frac{L/2}{D_{\text{ш}}}+\frac{\Delta h}{D_{\text{ш}}};$$

$$t_{\text{зар}}=\frac{l}{D} \quad [\text{ш} = \text{c} = \text{cord}]$$

and

$$t_{\text{п}}=\frac{L/2}{D_{\text{ш}}}-\frac{\Delta h}{D_{\text{ш}}}.$$

Inasmuch as

$$t_{\text{л}}=t_{\text{зар}}+t_{\text{п}},$$

will obtain

$$\frac{L/2}{D_{\text{ш}}}+\frac{\Delta h}{D_{\text{ш}}}=\frac{l}{D}+\frac{L/2}{D_{\text{ш}}}-\frac{\Delta h}{D_{\text{ш}}},$$

whence

$$2\frac{\Delta h}{D_{\text{ш}}}=\frac{l}{D},$$

or

$$D=D_{\text{ш}}\frac{l}{2\Delta h}. \tag{4.39}$$

For determination of the unknown speed D it is necessary and sufficient to know the magnitude of l, Δh and the speed of detonation of the cord D_c. The value D_c can be determined by one of the described below methods. It is clear that the detonating cord should possess a high constancy of speed of detonation for various sections of the same batch.

During determination of the speed of detonation by this method charges with an overall length of 30-40 cm with a length of the base l = 20-25 cm are used. Under these conditions errors of a single measurement constitutes 3-5%.

In spite of low accuracy, obtained for charges of significant length, the Dotrish method is widely used in contemporary research. The possibility of application of this method under field conditions is especially valuable, where it is not always possible to use methods, requiring exact electronic or optical equipment. In laboratory conditions the Dotrish method is replaced by other, more exact methods.

2. Photographic Method

Photographing of the luminescene accompanying propagation of detonation by charge of explosive is the most wide-spread. For photographing instruments are used, called photoregisters, or photochronographs. There are two types of photoregisters, 1) photoregisters (photochronographs) with an unrolling drum and 2) photoregisters with an unrolling mirror.

Instruments of the unfolding drum started to be used at the end of past century; at the present these instruments everywhere have been displaced by instruments of the unfolding mirror, having a number of essential advantages and first of all large resolution in time.

Figure 4.45 gives the fundamental system of a photoregister of the drum type. On drum 1, which can revolve with great speed around the vertical axis, the photographic film is secured. Between charge of the explosive 2 and lens 3 is usually located a narrow vertical slot 5. The relation of the magnitude of the lens to the magnitude of the image is designated as K, i.e., the degree of decrease of the photographic system. If the charge has a length l, then the length of the image of charge l_{im} on the film will be $l_{im} = \frac{l}{K}$.

Figure 4.46 gives the system of recording. Let us assume that motion of film occurs from the left to the right with a speed v_{fi}.

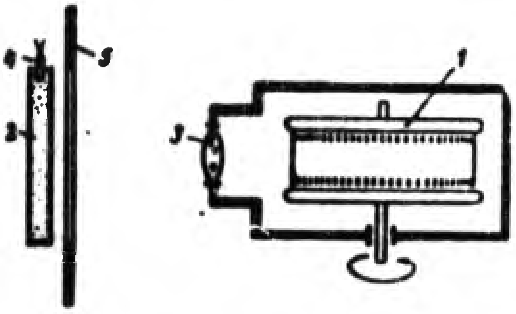

Fig. 4.45. System of photoregister of drum type for determination of speed of detonation. 1 – drum with photographic film; 2 – charge of explosive; 3 – lens of photoregister; 4 – percussion-detonator; 5 – slot.

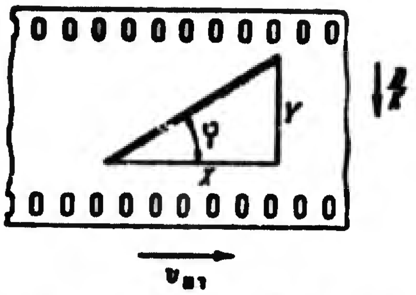

Fig. 4.46. System of recording of propagation of detonation on photoregister of drum type.

If the charge stands vertically and speed of detonation is D, then the image of the luminescene of detonation will shift also to the vertical (Fig. 4.46 shows down from above) with speed $\frac{D}{K}$. As a result of the addition of two mutual-perpendicular shifts we obtain a slanted line. Knowing v_{fi}, it is possible by the angle of inclination of this line to determine the value of D. Really,

$$\frac{D/K}{v_{\text{пл}}}=\text{tg}\,\varphi.$$

[пл = fi = film]

or

$$D=v_{\text{пл}}K\,\text{tg}\,\varphi. \qquad (4.40)$$

It is more convenient and more exact to measure not the angle φ, but directly the length of projections on the vertical Y and horizontal X axis,

$$\text{tg}\,\varphi=\frac{Y}{X}$$

and

$$D=v_{\text{пл}}K\frac{Y}{X}. \qquad (4.41)$$

Thus, for measurement of the speed of detonation by this method it is necessary to know: the length of projections Y and X (determined by means of photographic treatment with the help of a photographic enlarger, microscope, or other device), the value of K (determined by means of photographing at a given distance of the scale rod) and the speed of movement of the film v_{fl}, which may be estimated by means of drawing on the moving film images of flashes of known constant frequency (time mark).

There are various methods of obtaining of time marks. The method of measurement is very wide spread, at which an explosion is produced at a certain constant number of turns N^{*}. In this case

$$v_{fl} = LN^{*},$$

where L is the length of the circumference of drum. A constant number of turns is obtained either by using a synchronized motor, or, for instance, on the basis of a stroboscopic effect.

If on the shaft of the drum a circle with one radial line is set, then during illumination by a neon tube from a network of alternating current 50 cps, this circle will seem motionless, if the number of turns N^{*} is equal to 6000 rpm (i.e., 100 revolutions per second — the frequency of 50 cps gives 100 flashes per second), and also 12,000 rpm, etc. When the number of turns is somewhat below 6000 per minute, then it will seem that the circle slowly revolving to the side, opposite the direction of true rotation; if the shaft makes somewhat more than 6000 rpm, then it will seem that circle is slowly revolving in the direction of true rotation. Regulating the number of turns of the motor, in the moment of apparent stop explosion of the charge is produced.

For a photoregister of the drum type the speed of movement of the film usually is limited by the value $v_{fl} \overline{<} 100$ m/sec; with a high speed the film, fastened on the outside of the drum bursts. Somewhat high speed of recording can be carried out, if the film is fastened on the internal surface of the drum, using a mirror or prism for direction of beams from the lens to the film. However, at a peripheral velocity of 200-250 m/sec bursting of the drum itself is possible. The limiting speed of the film is also the most important deficiency of photoregisters with a revolving drum. For research of processes of detonation of condensed explosives this speed is insufficient.

Analysis of the conditions of measurement with the help of a photoregister of the drum type shows that the greatest accuracy is obtained with $\varphi = 45^{\circ}$, i.e., when $\frac{D}{K} \approx v_{fi}$. If the angle φ significantly differs from 45° and, in particular, if $\frac{D}{K} \gg v_{fi}$, then the accuracy of measurements sharply is lowered. Let us assume that it is necessary to measure the speed of detonation of the order of 8000 m/sec. Since the maximum value of $v_{fi} \approx 100$ m/sec, then for observance of the condition $\frac{D}{K} \approx v_{fi}$ it is necessary to take K in the order of 80, i.e., to obtain an image, almost 80 times smaller than the lens. In practice usually such distances and lens are used that $K \approx 20$-30; this means that a charge with a length of 20-30 cm will be designed on film as a section of a total of one cm. In addition, with great speed of detonation of the tested charge the angle φ will be obtained larger and for charges of significant length accuracy will be small.

Practically for charges with a length of 40-50 cm the error of separate measurement can constitute 2-5%, i.e., essentially we will obtain accuracy of the same order as according to the Dotrish method. A serious advantage of photoregister of the drum type over the Dotrish method is the fact that if the speed of detonation is variable, then this is easily established on the photograph by distortion of the image. In principle it is possible, conducting tangents, to calculate the speed of detonation on separate sections; however if these sections in accordance with the character of change of speeds is short, then the result of the measurements will be extremely unreliable. Thus, if drum photoregister can be used very successfully for determination, for instance, of the burning rate, then for research of detonation its resolving power is insufficient.

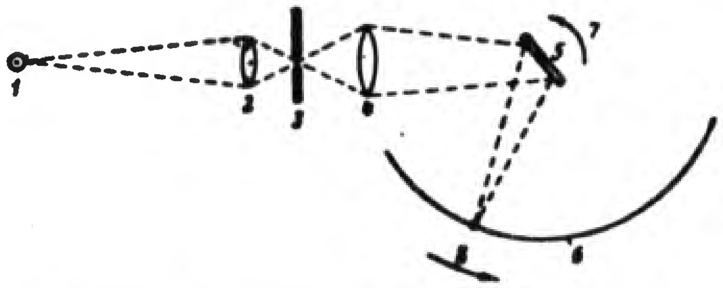

Fig. 4.47. System of photoregister with unfloding mirror. 1 — charge of explosive; 2 and 4 — lenses; 3 — slot; 5 — mirror; 6 — film; 7 — direction of rotation of mirror; 8 — direction of shift of image on film.

Figure 4.47 gives the fundamental system of a photoregister with an unflolding mirror. The charge of an explosive 1 is located perpendicular to the drawing plane; lens 2 gives a reduced image of the charge in the plane of slot 3; lens 4 with the help of mirror 5 projects this image on the film 6. The image on the film is usually somewhat decreased with respect to the natural magnitude of the charge. In an instrument of the unfolding mirror the film is secured motionless. Therefore, if detonation of charge spreads perpendicular to the drawing plane, then with a motionless mirror an image in the form of line will be obtained on the film, also perpendicular to the drawing plane. If the mirror revolves in the direction, shown in Fig. 7, then the image will shift in the direction, shown by Fig. 8, which also gives unfolding of the phenomenon in time. Thus, as in the case of a photoregister of the drum type, two mutual-perpendicular shifts will be obtained, which will give a slanted line on the film. Only now is the film motionless, and the image moves because of the turn of the light beam, evoked by rotation of the mirror. Figure 4.48 shows a sample of a photograph, obtained with the help of a photoregister of the mirror type.

If one were to designate by n the number of turns of the mirror per second and by R the distance from the mirror to the film, then the linear speed of unfolding v_1 will be equal to

$$v_{\text{л}} = 2 \cdot 2\pi R n = 4\pi R n.$$

An additional coefficient 2 enters in the expression for v_1 because the angular speed of rotation of the beam is two times higher than angular velocity of the mirror. Thus, the speed of unfolding is determined by the number of turns of the mirror and the distance from the mirror to the film.

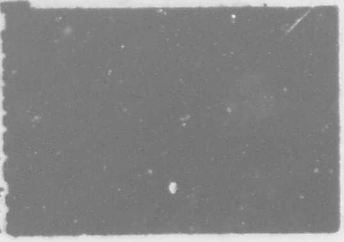

Fig. 4.48. Sample of a photograph on a photoregister of the mirror type. The slanted light band is the effervescence of detonation; the band of light on the left is the effervescence of expanded products.

At first sight it seems that the simplest method of increasing v_1 is a maximum increased R, however this is not so. Instruments with a large optical arm are inconvenient in operation and, mainly, worsen the clearness of the image, therefore the magnitude of R is usually taken as moderate. Thus, in a photoregister of the mirror type SFR, developed in the Institute of Chemical Physics of the Academy of Sciences of the USSR, the magnitude of R is near 24 cm. The number of turns of the small dimension light mirror may be very large. For instance, in the SFR instrument n = 1000 revolutions per second which with R = 24 cm gives v ≈ 3000 m/sec. This speed of unfolding considerably exceeds the maximum obtainable speed for a photoregister of the drum type. The speed of detonation is calculated by the formula, analogous to (4.41)

$$D = v_{\text{л}} K \frac{Y}{X} = 4\pi R n K \frac{Y}{X}. \qquad (4.41a)$$

In order to meet the condition $\frac{D}{K} = v_1$ — the condition of the least error (this condition pertains to photoregisters both drum, as well as the mirror type) even during measurement of the highest speeds of detonation of the order of 8-8.5 km/sec, it is sufficient to have $K \approx 3$. This makes it possible to decrease the length of the tested charges and sharply increases accuracy of measurements on separate sections in the case of detonation with variable speed.

The optical system of the instrument, including two lenses, makes it possible to obtain relatively small decreases (K = 3 to 5) with a significant distance between the charge and the lens (otherwise protection of the lens would be difficult; with a significant distance the lens is plane-parallel optical glass in the wall of the explosive chamber is reliably protected).

The system of two lenses is further convenient because the vertical slot cannot be disposed near the charge, but in a focal plane of the first lens.

For determination of v_1 there are various methods. The most accurate consists of the following. An electrical contour is created, in which rotation of the mirror evokes oscillation with a frequency equal to the frequency of rotation. These oscillations accumulate with oscillations of a crystal generator of strictly constant frequency. Depending on the relationship of frequencies various figures are obtained on the screen of an electron-tube, for instance, an ellipse with various number of indentations; a definite number of indentations corresponds to a fixed value of v_1. Near this value the projections revolve in that or another side (just as during a stroboscopic effect). The stop of motion on the screen means that a strictly definite speed of rotation of the mirror is attained and, consequently, a strictly definite v_1. At this instant an explosion is produced.

The majority of instruments of an unfolding mirror requires a special synchronizing device so that the moment of explosion coincided with a definite position of the mirror. By their system in Fig. 4.47 it is clear that by far an luminescence will not be fixed on the film in any position. The necessity of synchronization of the moment of explosion with a definite position of the mirror introduces certain complication, but it does not have an essential value as compared to those advantages, which the instrument gives. With use, for instance, fo the SFR instrument, it is possible to measure the speed of detonation of the base of 10-12 cm with a precision of separate measurement near one percent. Certain modification of the instrument allows obtaining instead of continuous unfolding in time of a series of separate photographs (frames), the following one after the other with a frequency up to $2 \cdot 10^6$ frames/sec. Samples of such photographs (magnified) are shown in Fig. 4.49.

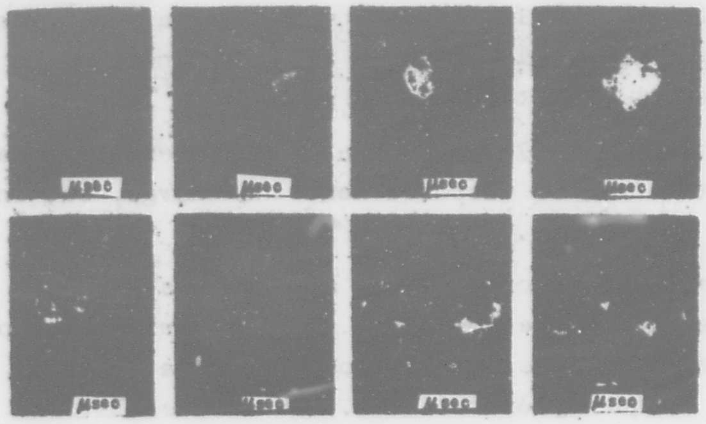

Fig. 4.49. Sample of photographs of detonation, obtained with the help of SFR-2 in a variant of time beams. The charge is in the form of a parallelepiped 30 × 76 × 120 mm. The lens is turned to the side 30 × 76. Photographs were produced in two microseconds. Imprints are given for the moments 8, 16, 24, 32, 48, 64, 80, 96 microseconds from the beginning of the explosion. Initiation is from above (in the middle). Below is a scale rule. The big division (light section of the biggest length) is 150 mm.

Photoregister of the mirror type is at present the basic instrument for exact measurement of the speed of detonation.

3. Oscillographic Method

The essence of the method consists of the following. In charge of an explosive two (or more) spark gap are disposed, on which a definite voltage is given. The explosive in the initial state (poured, pressed, powdered, liquid) possesses a minute conductivity, and current does not pass through the spark gaps.

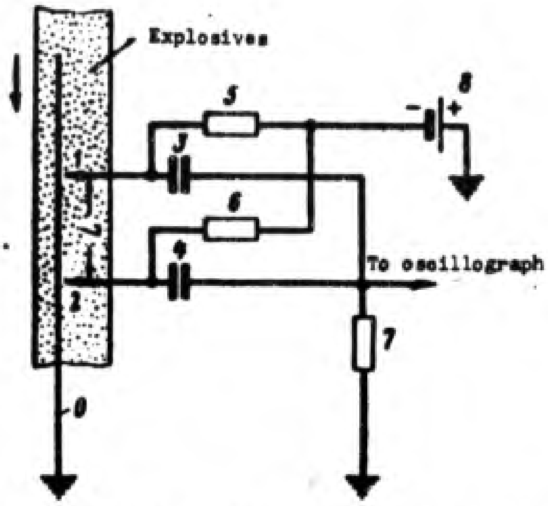

Fig. 4.50. System of oscillographic method of determination of the speed of detonation. 0 — ground wire; 1, 2 — spark gaps; 3, 4 — capacitors; 5, 6, 7 — resistors; 8 — source of constant voltage.

In the detonational wave products of the explosion are strongly ionized, their resistance is small (for products of explosion of typical explosives resistance constitutes near 10-20 ohm/mm), as a result during passage of the detonational wave spark gaps short circuit consecutively, in them current appears which is fixed by a cathode oscillograph.*

There are many systems, which can be used. Figure 4.50 gives one of the possible simple variants of the method.

In the charge of the explosive are two wires, ending in points, which with the ground wire 0 form spark gaps 1 and 2, being at a distance L from each other. The electrical circuit includes capacitors of small capacity 3 and 4, very large resistors 5 and 6, resistor 7 and source of voltage 8.

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*In many old methods moments of income of detonational wave were fixed by the break of wires, located in the charge. For measurements of great accuracy this method is not recommended. The appearance of a current in the spark gap during the income of the detonational wave is fixed significantly more exact than stopping the current during burst of the wire.

Before carrying out the experiment capacitors are charged from source 8 through resistors 5 and 6 and resistor 7. Let us assume that detonation spreads downwards. With closing of interval 1 capacitor 3 will start to discharge through resistor 7 and interval 1; in chain will appear a current of small duration (because of the small capacity of the capacitor). In a certain time the interval 2 , will be short circuitd the discharge of capacitor 4 will start and a second current pulse will appear.

Thus, with help of the given system (or other more complicated systems) during propagation of detonation in the electrical chain two consecutive current pulses are obtained, provoking corresponding jumps of voltage, which the cathode oscillograph also fixes.

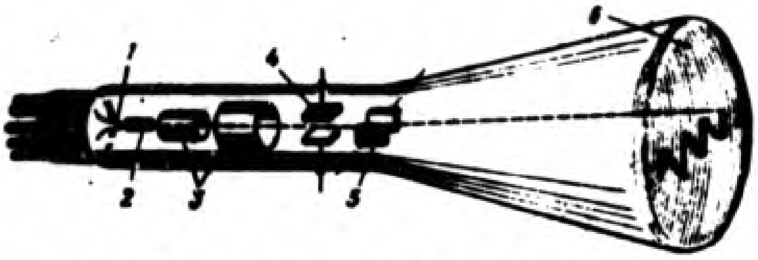

Fig. 4.51. System of electron-beam tube. 1 — cathode; 2 — grid; 3 — anodes; 4 — plates, deflecting the beam to a vertical plane; 5 — plates, deflecting beam to a horizontal plane; 6 — screen.

The basis of the cathode oscillograph is the electron-beam tube (Fig. 4.51). In the left part of the tube there is a device, which consists of a cathode, grid, and two anodes, which form a thin electron beam (shown in Fig. 4.51 by the dotted line). Falling on the screen, the electron beam evokes its luminescence in the form of a point, if beam is motionless, and in the form of a curve, if the beam deviates and moves along the screen of the tube. During movement of beam illumination in every point of the screen is very brief, but sufficient to photograph it with the help of the camera. The electron beam inside tube passes between two pairs of plates. The first pair of plates 4 during supply to them of voltage deflects the electron beam in a vertical plane; the second pair of plates 5 deflects the beam in a horizontal plane. Let us assume that on one pair of plates voltage moves, variable in time according to the rule, close to linear, then the beam will shift along screen with a constant speed. By such a simple method we ensure temporary unfolding. If on the other pair of plates jumps of voltage fall, for instance, obtained in the system of Fig. 4.50, then these jumps will unfold in time. During photographing of the screen of the oscillograph on still film we obtain a recording of the type depicted in Fig. 4.52. Frequent for such recordings double-beam oscillographs are used; a second beam (lower beam on Fig. 4.52) is used for drawing time marks. For that on the unfolding of the second beam, moving with the same speed as first, signals of strictly constant frequency pass, for instance, from a crystal oscillator.

The electrical circuit has a device for starting unfolding of the oscillograph which can be carried out with the help of an auxiliary transducer, located ahead of the basic working transducers.

Fig. 4.52. Image on film during oscillographic determination of the speed of detonation (diagram).

Comparing the distance between the two jumps of voltage with time marks, it is possible with great accuracy to determine the interval of time t between jumps, which in accordance with the above stated is equal to the interval of time between income of the detonational wave to the intervals 1 and 2 accordingly (see Fig. 4.50). If the distance L is measured beforehand, then

$$D=\frac{L}{t}. \qquad (4.42)$$

The use of a cathode oscillograph allows with high accuracy to determine the time t, therefore, also with high accuracy it is necessary to measure the distance L (up to the use of measuring microscope).

In the simple diagram, shown in Fig. 4.50, there are only two spark gaps. Somewhat complicating the diagram, it is possible to introduce many such intervals and to measure the speed of detonation on several sections of the charge, which is very important for transient detonation, proceeding with variable speed. (For obtaining n bases of measurement, obviously, it is necessary to have n + 1 intervals.)

Figure 4.50 shows only the fundamental diagram of ionization transducers in the form of spark gaps. In practice various constructions were used as ionized transducers (faces, needles, foils, etc.) depending on the state of the charge of the explosive (liquid, poured, pressed, powder).

Accuracy of the measurement of speed of detonation depends on the time of unfolding the cathode oscillograph. If, for instance, on OK-17, oscillograph is used for measurement of the speed of detonation, developed by the Institute of Chemical Physics of the Academy of Sciences of USSR, for which the minimum time of unfolding is 3 microsecond (i.e., in 3 microseconds the electron beam will pass the entire screen), then with a base of measurement of 2 cm (in the case of powerful explosives with a great density such a distance will be passed by a detonational wave approximately in 2.5 microseconds) the error will be in the order of one percent.

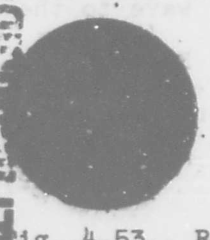

Fig. 4.53. Recording on film during determination of the speed of detonation on an oscillograph with spiral unfolding (diagram). 1 — first waste material; 2 — second waste material.

Even greater accuracy can be obtained, using an oscillograph with spiral unfolding, an example of which is the OK-15, oscillograph, also developed in the Institute of Chemical Physics of the Academy of Sciences of USSR. An example of recording is shown in Fig. 4.53. Unfolding goes by a spiral: jumps of voltage due to consecutive short circuiting of ionization intervals by the detonational wave give waste material in a radial direction. In this case, it is also possible to produce measurement on several consecutive bases.

For the OK-15, oscillograph a complete turn of the beam occurs in one microsecond; the angle $\frac{2\pi}{100}$, which can be measured very exactly corresponds to a time of 10^{-8} sec. With the help of the OK-15 oscillograph it is possible to measure the speed of detonation on the base of several millimeters with an error near one percent. When needed it is possible even to produce measurement on the base of several tenths of millimeter, but accuracy with this will be reduced.

The use of a cathode oscillograph for research of detonational processes and, in particular, for measurement of the speed of detonation still has not found wide application, but has exclusively more prospects. The method of the cathode oscillograph with respect to resolution in time exceeds the photoregister of the mirror type. This is especially essential during the study of transient conditions of detonation (near initiator, during transmission of detonation), scattering of products of explosion near the charge, initial motion of the medium contacting the charge, its initial mass speed, etc. Furthermore, the possibility of measurement of the speed of detonation on small bases sharply decreases the expenditure of explosives and facilitates laboratory research.

There is basis to assume that with further development and improvement of the shown method will replace photographic and will become the basic method for determination of the speed of detonation.

A unique compound of photographic and oscillographic methods is described in literature of the method of measuring the speed of detonation and research of explosive phenomena with the help of the

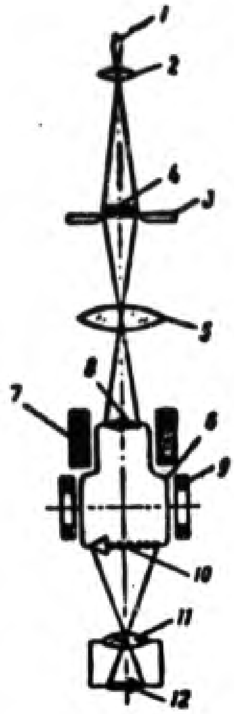

Fig. 4.53. Diagram of determination of the speed of detonation with the help of an electron-optical convertor. 1 — charge; 2 — lens ; 3 — slot; 4 — intermediate image in plane of the slot; 5 — second lense; 6 — tube of electron-optical converter; 7 — magnetic lens; 8 — second image on light sensitive cathode; 9 — deflecting coverings, giving unfolding in time; 10 — electron image on screen of converter; 11 — lense of camera; 12 — image on photographic film.

electronic-optical converter, a diagram of which is shown in Fig. 4.54. The electronic-optical converter is a cathode oscillograph, in principle analogous to the above mentioned, but with an electronic-beam, having a light sensitive cathode. During illumination of any point of the light sensitive cathode an electron beam starts to emerge from it, which is accelerated and is focused by corresponding devices inside the tube and falls on its fluorescent screen, where a luminescent point appears. During illumination of the surface of the cathode along line 8 on screen a luminescent line 10 appears. If between the system, focusing the electron beam and screen an electrical or magnetic field is created, then it is possible to deflect the electron beam and change the position of line 10. Creating along the path of electrons a field, the line changing in time, we obtain uniform temporary unfolding. When along line 8 the image of the luminescent point shifts (luminescence of detonation, spreading along the charge), then on screen a slanted straight line is obtained (with a constant speed of detonation) or a curve. The photographing screen on still film with an ordinary camera obtain a recording. The angle of inclination of the straight line (or angle of inclination of the tangent to the given point of the curve) is a measure of the relationship of the speed of the luminescent point by the cathode and speed of temporary unfolding. If the latter is known, and also optical data of the system is known, then it is possible with great accuracy to determine the speed of detonation. According to published data, such instruments allow the obtaining of resolution in time of the order of 10^{-9} sec, and less and determines the speed of detonation on sections in several tenths of millimeters. Modification of this part allows obtaining a series of separate frames, taken at an interval 10^{-6}-10^{-7} sec.

§ 11. Theory of Detonation of Gases

1. General Information

The first hypothesis advanced for an explanation of detonation in 1869, was the "theory of synchronous vibrations" of Abel. Abel considered that during an explosion in the environment oscillaton of a definite frequency for each explosive appears. These oscillations spread to all sides and if on their way an explosive is met, then the molecule of the latter, resonating, starts to oscillate. These oscillations lead to the appearance of reaction and explosion. Thus Abel explained the transmission of detonation in a distance. The hypothesis of Abel was also used to explain propagation of detonation in a solid mass of explosives. In this case the molecules, reacting as a result of resonance are in direct contact. Experimental research, set for checking the hypothesis of Abel did not confirm it as a result.

In particular it was shown that the transmission of detonation on a distance between charges from various explosives frequently by occurs easier than between charges of the same explosive, besides this, during excitation or transmission of detonation the magnitude of the exciting charge has a large value. Finally it was determined in many cases, when substance A (of large distance) transfers detonation well to substance B, and from B to A detonation is transmitted badly.

These and other facts, contradicting the hypothesis of Abel forced it to be refuted. As a replacement to the hypothesis of Abel in 1883, the "therory of blast wave" of Berthelot appeared.

We saw that propagation of burning of an explosive occurs as a result of the transmission from layer to layer of energy of the reaction in the form of heat by means of thermal conduction. To process of detonation these ideas are not applied to the process of detonation, since the speed of propagation of the order of thousands of meters per second characteristic for detonation as considered, cannot be ensured by energy transfer by means of heat transfer. Therefore, for detonation Berthelot took his own theory of another mechanism of energy transfer from layer to layer, which can ensure incomparably faster propagation of transformation.

According to Berthelot, during the action of an initial impulse, provoking detonation directly, for instance a percussion-detonator, or the explosive gas mixture there compression of a layer of the mixture as the first stage as a result of striking the products of the explosion capsule, being under great pressure. Due to rapid compression the layer of gas adiabatic is heated to a very high temperature. The high temperature in turn conditions a high speed of reaction. Since the reaction is exothermic and products of it are gases then as a result of the rapid transformation a sharp increase of the pressure in the reacting layer appears. This pressure, acting on the neighboring layer, evokes its compression with subsequent heating up and rapid chemical reaction, etc. Thus, the reaction spreads from layer to layer by means of a triple cycle of phenomena: mechanical (compression), thermal (heating up) and chemical (reaction). Inasmuch as energy transfer by means of shock compression occurs much faster than heat transfer, then the process in this case spreads with a speed many times greater than during burning.

The quantitative theory of propagation of a detonational wave was developed chiefly by French and Soviet researchers and is known by the name of the hydrodynamic theory of detonation.

This theory considers propagation of detonation as propagation of a rapid charge of pressure (shock wave). With this it is assumed that propagation of the rapid change of pressure evokes in the explosive system a rapid exothermic reaction the energy of which in turn supports stationary propagation of the shock wave. Thus, the speed of detonation is identified with the speed of the shock wave in the given system. Therefore, consideration of the hydrodynamic theory of detonation will be started from the hydrodynamic theory of the shock wave. Here we will consider shock waves and detonation mainly in gaseous systems. The theory of detonation of condensed explosives is presented in Section 12.

2. The Hydrodynamic Theory of Shock Waves

The forthcoming are elementary bases of the hydrodynamic theory, we will use the simplest method of conclusion of basic relationships, applied by Ya. B. Zel'dovich and A. S. Kompaneyts.

Let us assume (see Fig. 4.55) that in a tube with the section S, filled with gas a piston moves with constant speed w. By the action of the piston in the gas a shock wave appears — the region of compression spread in the undisturbed gas. In front of the shock wave front an intermittent change of pressure; density and temperature of gas occurs. The gas compressed by the piston will move with the speed of the piston, i.e., with a speed w; the front of the shock wave (front boundary of the region of compression) will spread in the undisturbed gas with

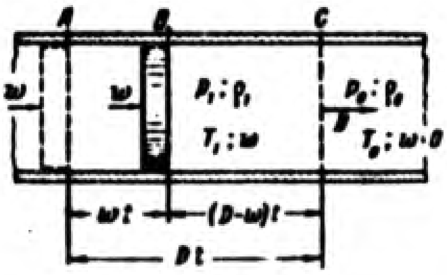

Fig. 4.55. Explanatory diagram at the conclusion of fundamental equations of hydrodynamic theory.

a speed D, larger than w while subsequently will be proved. Let us assume that in the initial moment the piston was in plane A, in an interval of time t the piston will be in plane B. The front of the shock wave in the initial moment was also in plane A; in the moment t it is in plane C: p_0, ρ_0 and T_0 are designated as the corresponding pressure, density and temperature of the gas in the initial state, and p_1, ρ_1 and T_1 — the pressure density and temperature of the gas, compressed by the shock wave. From Fig. 4.55 it follows that if during time t the piston passes distance wt, then the shock wave has passed distance Dt; the distance between the piston and the front of the shock wave front becomes (D - w)t. Hence the volume of compressed gas is equal to (D - w)tS, and the initial volume of the same quantity of gas is DtS. The mass of compressed gas is equal to ρ_1(D - w)tS, and the mass of gas before compression is equal to ρ_0DtS. Since in the process of compression the mass of the substance is not changed, then

$$\rho_0 DtS = \rho_1 (D - w) tS,$$

or

$$\rho_0 D = \rho_1 (D - w). \tag{4.43}$$

Equation (4.43) constitutes the law of conservation of mass during compression.

The compressed gas moves with a speed w and, consequently, during compression of the mass ρ_0DtS obtains the momentum ρ_0DtSw. According to the second law of Newton the change of momentum is equal to the impulse power, i.e., the product of force for the time of its action. The resultant force, effective on the gas between the piston and plane C, is equal to $(p_1 - p_0)S$, and its impulse during the time t is equal to $(p_1 - p_0)St$. Equating the change of momentum to the magnitude of the impulse, we obtain

$$(p_1 - p_0) St = \rho_0 DtSw,$$

or

$$p_1 - p_0 = \rho_0 Dw. \qquad (4.44)$$

Equation (4.44) constitutes law of conservation of momentum during compression.

Now we will write an equation of energy conservation during compression. Consider that during compression a gas does not issue and does not obtain heat from without, therefore, the change of its total energy should be equal to the performed above gas operation work. In turn, total energy is composed of internal (thermal) energy and the kinetic energy of moving gas. We will designate as ε_0 and ε_1 the initial and finished specific internal energy (i.e., internal energy of mass unit); the kinetic energy of the mass unit of compressed gas is obviously equal to $w^2/2$. Since the mass of compressed gas is $\rho_0 DtS$, then a complete change of energy of gas during compression will constitute $\rho_0 DtS(\varepsilon_1 - \varepsilon_0 + w^2/2)$. Work of external force in the gas is the work of the piston effective on gas with a force of $p_1 S$ by way of wt. Equating the measurement of the energy to work of the force and reducing to tS, we obtain

$$\rho_0 D\left(\varepsilon_1 - \varepsilon_0 + \frac{w^2}{2}\right) = p_1 w. \qquad (4.45)$$

Equation (4.45) essentially constitutes the law of conservation of energy during compression.

Joining to the three written equations of the preservation (4.43)-(4.45) an equation of the state of gas, one can determine any of five magnitudes p, ρ, T, w and D, if one of them is given and the initial parameters of the gas p_0, ρ_0 and T_0 are known.

Above we gave the simplest conclusion of fundamental equations of the hydrodynamic theory of shock waves with use of a moving piston. But also not resorting to this method, an equation can be concluded simply from the law of conservation of mass momentum and energy during transition through a front of a shock wave. With such conclusion it is very convenient to use a coordinate system, moving with the speed D, i.e., a system in which the front of the shock wave is motionless. In such a coordinate system the undisturbed gas will flow in front of the shock wave front with a speed of D and ensue from it with a speed of D - w.

The equating the flowing and ensuing flows of the substance, momentum and energy, we obtain relationships, analogous to the equations (4.43), (4.44) and (4.45).

Thus, for instance, in the front of a shock wave front a quantity of substance $D\rho_0$ flows, and ensues $(D - w)p_1$. From the law of conservation of mass we directly obtain the relationship (4.43).

Up to now, we have been talking about a shock wave, but everything that has been said also pertains to a detonational wave; this is a shock wave which accompanies a fast chemical reaction.

Equations of the conservation of mass and momentum for shock and detonational waves are absolutely identical. With a composition of the equation of energy conservation in the case of detonational waves it is necessary to add q — the specific heat of explosion of the thermal part of internal energy, i.e., potential chemical energy separated in front of the detonational wave. Thus, for an ideal gas in the case of a shock wave

$$e_0 = c_v T_0,$$

and in the case of a detonational wave

$$e_0 = c_v T_0 + q.$$

With the conclusion of equations it is usually assumed that the basic parameters of a shock wave in the front preserve constant values. In reality, as we will see further for real shock waves of an explosive, the pressure, temperature, density and speed of flow in the front drop rapidly. In the case of such shock waves the introduced equations are accurate with respect to the values of corresponding parameters (p, ρ, t) in the front of the wave. In order to underline this circumstance in technical literature corresponding magnitudes frequently have the subscript "f" (p_f, ρ_f, T_f); we will as before use the adopted symbols p_1, ρ_1, T_1, carrying these values to the front of the shock wave.

Let us consider the basic conclusions following from the two first conservation laws (the law of conservation of mass and the law of conservation of momentum). These laws are identical both for shock and for detonational waves during any equation of the state, therefore, the conclusions of them are also universal.

First of all directly from the equation of the conservation of mass (4.43) we obtain for the speed of flow

$$w=\frac{\rho_1-\rho_0}{\rho_1}D. \qquad (4.46)$$

Since a substance in a shock wave is compressed ($\rho_1 > \rho_0$), then $w > 0$ and is directed to the same side as D. From the other side, $\rho_1 - \rho_0/\rho_1 < 1$ and $w < D$. Thus, a result of the law of conservation of mass during compression in shock wave is the appearance of the flow of a substance in the front of a shock wave, moving in the direction of propagation of the wave.

Exclusively important is the relationship (4.44), according to which excess pressure on the front of the shock wave is equal to the product of the initial density of the medium the speed of propagation of the front of the shock wave and the speed of the flow of the substance directly in the front of the wave. This relationship, based on the fundamental law of mechanics is accurate for shock, as well as for detonational waves. In the latter case ρ_0 constitutes the initial density of the explosive, and D — the speed of detonation.

For very strong shock waves (and practically always for detonational waves) $p_1 \gg p_0$, therefore, the value p_0 can be disregarded. Then

$$p_1 = \rho_0 D w. \qquad (4.44a)$$

The relationship (4.44) and (4.44a) make it possible by experimental means to estimate the magnitude of the pressure on the front of the detonational wave (see p. 356). To determine ρ_0 is very simple. With great accuracy it is also possible to determine D – the speed of detonation. The speed of the flow in the front of wave w is significantly more difficult to determine. However, recently in literature a number of methods have been shown, which resolve this problem and give a reliable appraisal of the value of the magnitude of w. According to certain of these methods the speed of products of detonation are measured directly according to others – the magnitude of w is estimated indirectly according to the character of the influence of the detonational wave on the medium in direct proximity of the surface of the explosive.

We will note one circumstance, which we will require subsequently. From general physical relationships ensue that the dimension of pressure ($L^{-1}Mt^{-2}$) and the dimension of energy of unit of volume are identical,

$$\frac{MLt^{-2}}{L^2} = \frac{ML^2t^{-2}}{L^3} = ML^{-1}t^{-2};$$

their numerical value differ in a dimensionless coefficient.

In the case of an ideal gas its internal energy is

$$E = \frac{pv}{k-1},$$

where

$$k = \frac{c_p}{c_v}.$$

Hence the internal energy of the unit of volume is

$$e_v = \frac{p}{k-1}.$$

Thus, knowing the pressure of detonation ($p_1 = \rho_0 Dw$), it is possible also to estimate the magnitude of internal energy of the unit of volume in a detonational wave. For that it is necessary to multiply the value of the pressure by the coefficient 1/k-1.

We will further conduct certain relationships which we will need subsequently. From the fundamental equations (4.43) and (4.44) can be obtained an expression for D and w, placing in them the volume of the mass unit $v = 1/\rho$:

$$\frac{D}{v_0} = \frac{D - w}{v_1}; \qquad (4.47)$$

$$p_1 - p_0 = \frac{Dw}{v_0}. \qquad (4.48)$$

From (4.47) can be obtained

$$w = D\frac{v_0 - v_1}{v_0}, \qquad (4.47a)$$

or

$$D = \frac{v_0}{v_0 - v_1} w. \qquad (4.47b)$$

Putting these values of D or w in (4.48), we obtain

$$D^2 = v_0^2 \frac{p_1 - p_0}{v_0 - v_1}; \qquad (4.49)$$

$$w^2 = (p_1 - p_0)(v_0 - v_1). \qquad (4.50)$$

We will find now the relationship between the pressure and specific volume in the shock wave. For an ideal isentropic process the connection between the pressure and volume is given in the adiabat equation of Poisson

$$pv^k = \mathrm{const},$$

where

$$k = \frac{c_p}{c_v}.$$

This equation, assuming the constancy of entropy, is inapplicable to shock waves: one of the most important properties of a shock wave is the fact that in it because of irreversible losses of energy during the transition through a rapid change entropy increases more significant the stronger the wave.

From equation (4.45), replacing ρ_0 by $1/v_0$, we obtain

$$\frac{D}{v_0}\left(e_1-e_0+\frac{w^2}{2}\right)=p_1 w. \tag{4.51}$$

Placing in this equation the value of D from (4.49) and the value of w from (4.50), after simple transformations we find

$$e_1-e_0=\frac{p_1+p_0}{2}(v_0-v_1). \tag{4.52}$$

If the thermodynamic properties of the substances are known, then it is possible to express specific energy as function of the pressure and the volume of the mass unit

$$e_1=f(p_1,\ v_1)$$

and

$$e_0=f(p_0,\ v_0).$$

Putting these values in (4.52), we obtain an equation of a certain curve, passing through point p_0, v_0 and giving the sought for connection of p and v. This curve is called the shock adiabat or dynamic adiabat, or the adiabat of Hugoniot.

Let us consider the case of a theoretical gas with a constant specific heat, for which

$$k=\frac{c_p}{c_v}=\text{const.}$$

Internal specific energy of such a gas is

$$e_1=\frac{p_1 v_1}{k-1} \text{ and } e_0=\frac{p_0 v_0}{k-1}.$$

Placing thse values in the equation (4.52), after simple conversion we obtain

$$\frac{v_1}{v_0}=\frac{\rho_0}{\rho_1}=\frac{(k-1)p_1+(k+1)p_0}{(k+1)p_1+(k-1)p_0}, \tag{4.53}$$

or

$$\frac{p_1}{p_0}=\frac{(k+1)\rho_1-(k-1)\rho_0}{(k+1)\rho_0-(k-1)\rho_1}. \qquad (4.53a)$$

Once again we underline that the equation of dynamic adiabat in the form of (4.53) or (4.53a), giving the simple connection between the values p and v (or p and ρ), is given for a theoretical gas on the assumption that k = const. If $p_1 >> p_0$ then disregarding in equation (4.53) the value of p_0 as compared to p_1, we obtain a limited increase of the density in a strong shock wave

$$\frac{\rho_1}{\rho_0}=\frac{k+1}{k-1} \qquad (4.54)$$

or

$$\frac{v_1}{v_0}=\frac{k-1}{k+1}. \qquad (4.54a)$$

Figure 4.56 gives a diagram of p - v for an isentrope (adiabat of Poisson, curve 1) and dynamic adiabat (curve 2) with the condition of an identical initial state of p_0, v_0, and k = 1.40 (air has such a value of k at moderate compressions). As can be seen the dynamic adiabat goes steeper than the isentrope. During an identical decrease of volume on the shock adiabat the pressure increases to a more significant degree. In the case of the isentrope an infinitely large pressure is attained with an infinitesimal specific volume (i.e., with an infinitely large density). In the case of the dynamic adiabat an infinitely large pressure is obtained with a value of $v_1 = \frac{k-1}{k+1} v_0$ (shown by the dotted line). The expression for the limiting value of the volume of the unit of mass with $p_1 \to \infty$

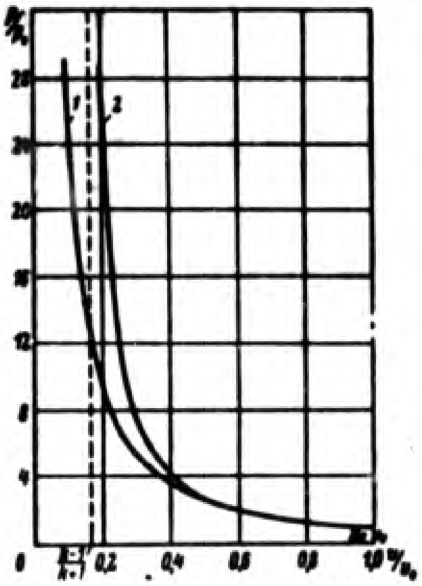

Fig. 4.56. Comparison of the adiabat of Poisson (1) and the adiabat of Hugoniot (2).

$$v_1=\frac{k-1}{k+1}v_0$$

can be used for deviation of several important relationships, which are accurate for strong shock waves. Substituting this expression in the formula (4.49) and disregarding the magnitude of p_0 as compared to p_1 we obtain

$$D^2 = \frac{k+1}{2} p_1 v_0.$$

Producing analogous substitution in (4.50) we find that

$$w^2 = \frac{2}{k+1} p_1 v_0.$$

Hence it directly follows that

$$w = \frac{2}{k+1} D. \tag{4.55}$$

Applying the relationship (4.44a), easily obtains

$$p_1 = \frac{2}{k+1} \rho_0 D^2. \tag{4.56}$$

We will underline once again that the equation (4.53)-(4.56) pertain to strong shock waves in a theoretical gas.

One should not think that with compression in a shock wave from p_0, v_0 to a certain state of p_1, v_1 are passed all intermediate points on the dynamic adiabat, in reality the substance by a sudden change passes from the condition p_0, v_0 of the state p_1, v_1. The wave with other pressure also suddenly will transfer the substance to other point p_1', v_1'. Curve of dynamic adiabat constitutes a locus of points, meeting conditions, obtained from the given initial state with a single compression by shock waves of various intensity.

3. The Hydrodynamic Theory of Detonational Waves

Up to now we have considered conclusions of hydrodynamic theory basically in reference to shock waves. We will stop now on conclusions specially pertaining to detonational waves.

Let us consider the case, when a shock wave spreads along a system, able to react extremely fast under action of rapid change of pressure (explosive gas mixture, explosive). The initial state of the system we characterize (as earlier) by the initial pressure p_0 and initial specific volume v_0. Under the action of a shock wave the state of the parent substance by a rapid change is changed and corresponds to point p_1, v_1 of the dynamic adiabat (Fig. 4.57). The speed of change of the state in a strong shock wave is so great that approximately the transition from the state p_0, v_0 of the state p_1, v_1 can be considered instananeous.

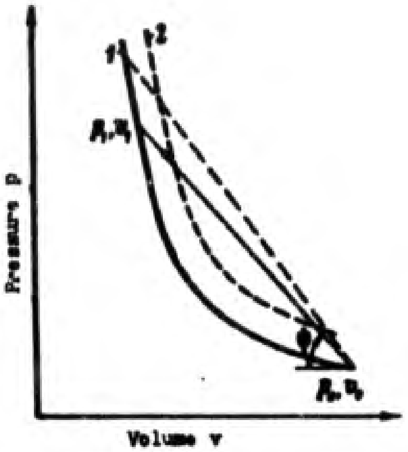

Fig. 4.57. Measurement of the state on the diagram p-v by means of passage of the reaction. 1) shock adiabat for initial explosive; 2) the same, for the condition, when part of the explosive has already reacted.

In the compressed substance a chemical reaction starts, which passes, although very fast, but not instantly. The reaction can appear, for instance because of intensive heating up evoked by compression. By means of the passage of the reaction the property of the substance will be changed and will emit heat.

Let us assume that in a certain time the reacted part of the substance also separated a definite quantity of heat Δq. With this the state of the system will be described as no longer adiabat for parent substance, but somewhat of another adiabat. Inasmuch as in system heat was separated this adiabat will lie higher than the adiabat of the parent substance (dotted line on Fig. 4.57). The change of state during the transition from the adiabat for parent substance to the dotted adiabat is not arbitrary but strictly definite. If the process of detonation is a stationary establishment, then transition from the initial adiabat to the dotted adiabat should be accomplished along a direct line, connecting the point p_1, v_1 and p_0, v_0, as shown by the pointer on Fig. 4.57. In order to prove this we will turn to the expression (4.49) for the speed of shock waves as a function of pressures and specific volumes

$$D^2 = v_0^2 \frac{p_1 - p_0}{v_0 - v_1}.$$

Let us note that the relation $p_1 - p_0 / v_0 - v_1$ is tg ψ — the tangent of the angle of inclination of the straight line, connecting points p_1, v_1 and p_0, v_0. Thus, the speed of detonation is proportional to $\sqrt{\text{tg}\ \psi}$. Every straight line conducted from the points p_0, v_0, will correspond to the speed of detonation. On the dotted straight line of Fig. 4.57 the speed will be more than on the solid.

The state of p_1, v_1 on the diagram of Fig. 4.57 corresponds to the front of the shock wave and spreads on the substance with a speed D. It is obvious that during stationary detonation all other intermediate states have to spread with the same speed, corresponding to the yield of that or another share of the total energy of the reaction. This means that the change of state in the process of chemical reaction should go by a straight line, connecting the points p_1, v_1 and p_0, v_0; only on this straight line all intermediate states spread on the substance with the same speed D as that of the front of the wave. Otherwise we would arrive at a position, at which the head part of the detonational wave (the front of the shock wave front) would spread with one speed, and that zone of the detonational wave where the reaction occurs — with another speed. Obviously, this process cannot be stable. Let us note that in the diagram p-v is a straight line of equal speeds of propagation by which the transition from one adiabat to another is accomplished, described by the equation

$$p = p_0 + \frac{D^2}{v_0^2}(v_0 - v) \qquad (4.57)$$

and is called the Michelson straight line.

Let us consider now the condition of transition from the adiabat of Hugoniot for the parent substance to an adiabat for final products, corresponding to full completion of the reaction and yield of full heat (Fig. 4.58). For clarity we will expound at first the actual position of things, i.e., without proof we will show, what form the transition from the adiabat of the parent substance to adiabat of products occurs. Proof that the other transition is impossible, will be given below.

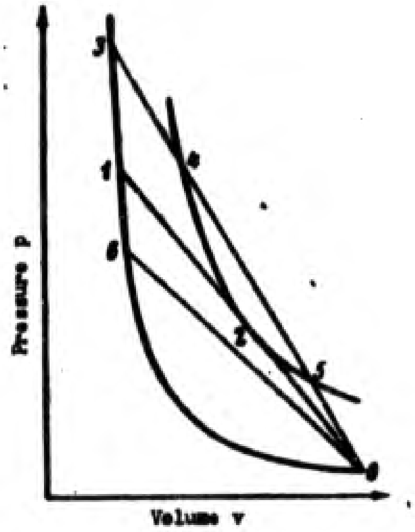

Fig. 4.58. Transition from adiabat of parent substance to adiabat of products of detonation. 0-6-1-3 — adiabat of Hugonoit for parent substance; 5-2-4 — the same, for final products of the reaction, point 0 — state of parent substance.

In the case of stable normal detonation as a result of the compression of the parent substance in a shock wave the state of it will correspond to point 1 (see Fig. 4.58) for which the straight line of Michelson, conducted between points p_1, v_1 and p_0, v_0, touches the adiabat of products of the reaction. By means of passage the reaction state of the substance is changed by this straight line 1-2-0. The point of tangency 2 corresponds to the final state of products of detonation after completion of chemical transformation and yield of full heat. The point of tangency is frequently called the Jouguet point.

As already noted, the expressed affirmation needs proof. It is obvious that the parent substance cannot be compressed to a state lying on the adiabat 0-1-3, lower than point 1; the corresponding straight line of Michelson (for instance, the straight line 0-6), by which as we saw the state should be changed, does not fall on the adiabat of final products. One would think, however, that the parent substance may be compressed to any state, meeting the points located on an adiabat higher than point 1, for instance to state 3, and transition from the adiabat of the parent substance to the adiabat of products can besides the tangent, be carried out by an infinite quantity of straight lines of Michelson which are secants of the adiabat of final products one of which (straight line 3-4-5-0) is given in Fig. 4.58. Every secant corresponds to its own speed of detonation (we will remind once again that the speed of propagation is proportional to the tangent of the angle of inclination of a corresponding straight line). Thus, one would think that there are possibly an infinite number of stable speeds of detonation. Meanwhile experiments show that in reality only the speed characteristic for a given system is stable. From all possible speeds it is necessary to select the only realized speed. Let us note that from all straight lines of the type 3-4-5-0 the tangent has least value of the tangent has least value of the tangent and, consequently, the transition by tangent corresponds to the least speed of propagation of detonation. In the initial period of development of hydrodynamic theory it was actually postulated that from all possible speeds of detonation in reality the least speed, corresponding to transition by tangent is carried out. At present there is strict proof of this postulate, given by Zel'dovich, which will be briefly presented subsequently.

We will stop now on several important properties of the point of tangency. The condition, which corresponds to the point of tangency will be designated as index "2" (p_2, ρ_2, v_2, T_2). This condition, in which products of an explosion are found instantly after completion of a chemical reaction, essentially differs from the state of a parent substance, compressed by a shock wave (point 1 on Fig. 4.58). Directly from Fig. 4.58 it is clear that

$$p_2 < p_1 \text{ and } v_2 > v_1.$$

The process of chemical transformation in a detonational wave is accompanied by expansion of the substance and a fall of pressure. The highest pressure is attained in the parent substance; by means of passage of the reaction and liberation of heat the pressure drops and after completing the reaction turns out to be significantly smaller than in a compressed parent substance. To this important and somewhat unexpected conclusion of hydrodynamic theory we will return further.

At the point of contact we get into the adiabat of Hugoniot for products, corresponding to full liberation of heat. The conditions, meeting points, located on the tangent between 1 and 2, in general, will be described by other adiabats, corresponding to smaller liberation of heat. However, it is necessary to underline the following. With an infinitesimal shift on the straight line near the point of tangency the straight line will separate from the curve by an infinitely small 2-nd order values. From this it follows that with such shifts the thermal effect also infinitesimally differs from the full thermal effect (obtainable on the curve). But this means that entropy increased by measure of the shift along the straight line 1-2 and attaining maximum at the point of contact with infinitesimal shifts near point of tangency is also not changed. And this in turn means that near the point of tangency the adiabat of Hugoniot coincides with the isentropic curve (i.e., with the adiabat of Poisson). This circumstance leads to a very important conclusion. The condition of contact can be recorded in the following form,

$$\frac{p_2-p_0}{v_0-v_2}=-\left(\frac{dp}{dv}\right)_2.$$

Inasmuch as at the point of contact the adiabat of Hugoniot coincides with an isentropic curve

$$\left(\frac{dp}{dv}\right)_2=\left(\frac{\partial p}{\partial v}\right)_s.$$

where $\left(\frac{dp}{dv}\right)_2$ and $\left(\frac{\partial p}{\partial v}\right)_s$ are corresponding angles of inclination of tangents at point 2 to the adiabat of Hugoniot and isentropic, consequently,

$$\frac{p_2-p_0}{v_0-v_2}=-\left(\frac{\partial p}{\partial v}\right)_s. \qquad (4.58)$$

Using the expression (4.49), for speed of detonation we obtain

$$D=v_0\sqrt{\frac{p_1-p_0}{v_0-v_1}}=v_0\sqrt{\frac{p_2-p_0}{v_0-v_2}}=v_0\sqrt{-\left(\frac{\partial p}{\partial v}\right)_s}.$$

From the equation of the conservation of mass (4.43) it follows that

$$v_0=\frac{D}{D-w_2}v_2,$$

where w_2 — pertains to point 2 in Fig. 4.58. Excluding v_0, we obtain

$$D-w_2=v_2\sqrt{\frac{p_2-p_0}{v_0-v_2}}=v_2\sqrt{-\left(\frac{\partial p}{\partial v}\right)_s}= \qquad (4.59)$$
$$=\sqrt{\left(\frac{\partial p}{\partial \rho}\right)_s}=\sqrt{k\frac{p_2}{\rho_2}}.$$

Magnitude of $\sqrt{\left(\frac{\partial p}{\partial \rho}\right)_s}=\sqrt{k\frac{p_2}{\rho_2}}$ is the local speed of sound c_2, i.e., the speed of sound in products of the explosion, at the point of contact, immediately after completion of the reaction.

Thus,

$$D-w_2=c_2, \tag{4.60}$$

or

$$D=w_2+c_2. \tag{4.60a}$$

Let us remember that the magnitude $D - w_2$ constitutes the speed with which the detonational wave spreads regarding products of explosion, which themselves move with the speed w_2.

According to the expression (4.60) which is a result of the condition of contact the speed of propagation of detonation regarding products is equal to the local speed of sound in products of the reaction.

Now it is possible in the form of a short diagram to expound the consideration of Zel'dovich, according to which the point of tangency indeed corresponds only to stable conditions.

Let us assume again that the transition from adiabat for a parent substance to adiabat for products is accomplished along straight line 3-4. It is possible to show that at point 4 just as in any point, lying above the point of tangency the local speed os sound $c_4 > D - w_4$. However, after the detonational wave there is a wave of rarefaction, which, as with all waves of rarefaction, spreads with the local speed of sound i.e., in this case with a speed c_4. Since $c_4 > D - w_4$, then the wave of rarefaction will overtake the detonational wave, will weaken it, will decrease the pressure and will decrease the speed of propagation; therefore, conditions corresponding of the state at point 4, cannot be stable. If we even managed, for instance, with the help of a very strong initiator to create in the substance a detonational wave, spreading with a speed larger than the stable speed of detonation inherent in it, corresponding to the tangent then the speed would rapidly fall to this normal value.

The secant intersects the adiabat of products also at point 5. However, it is easy to show that the state, corresponding to point 5, cannot be attained. The fact is that in point 5 it is possible to get just descending from above along the secant starting from point 3 through point 4. But point 4 already corresponds to full liberation of heat. Since below point 4 the secant lies to the right of the adiabat of products then for transition from point 4 to point 5 along a straight line it would be required to transmit by products an additional quantity of heat over and above the full heat, which is emitted during chemical transformation. This also shows that the realization of conditions, corresponding to point 5, is impossible.

Thus, the only state obtainable at point 2 at the point of contact, which corresponds to the minimum speed of detonation is stable. At the point of contact $c = D - w$ a wave of rarefaction spreads products of the explosion with the same speed as the detonational wave regarding products. With this the wave of rarefaction will go exactly in the state meeting point 2 not outstripping it and not lagging.

The point, meeting the state of the substance, compressed by a shock wave, should lie on one straight line of Michelson with the point of tangency. It is obvious that this condition corresponds to point 1. In the process of propagation of a stable detonational wave such conditions are exactly established, at which the parent substance is compressed to the state at point 1, and then, by measure of the growth of the reaction along a straight line (tangent) passes into a state, corresponding to point 2.

As a result of the selection of an infinite number of speeds as the only real speed we essentially obtained fifth equation (in addition to the three equations of preservation and equation of state). This equation may be used both in the form of a condition of contact (4.58), as well as in the form of a result of this condition (4.60).

The presence of five equations allows simply to determine five unknowns of magnitudes (p_2, ρ_2, T_2, w, and D) under the condition that the initial state and specific heat of explosion is given. Let us give the expression for the speed of detonation in two variants.

First of all according to (4.58) we have

$$\frac{p_2-p_0}{v_0-v_2}=-\left(\frac{\partial p}{\partial v}\right)_s=k\frac{p_2}{v_2}. \qquad (4.58a)$$

In the case of detonational waves $p_2 \gg p_0$. If p_0 is disregarded as compared to p_2, then

$$\frac{p_2}{v_0-v_2}=k\frac{p_2}{v_2},$$

or

$$\frac{1}{v_0-v_2}=\frac{k}{v_2},$$

hence

$$v_2=\frac{k}{k+1}v_0. \qquad (4.61)$$

Putting (4.58a) in (4.49), we find

$$D^2=v_0^2\frac{kp_2}{v_2},$$

or

$$D=\frac{v_0}{v_2}\sqrt{kv_2p_2}$$

According to the equation of the state of a theoretical gas

$$p_2v_2 = nRT_2,$$

where n is the number of moles per unit of weight.

On the basis of (4.61)

$$\frac{v_0}{v_2} = \frac{k+1}{k},$$

whence

$$D = \frac{k+1}{k}\sqrt{knRT_2}. \qquad (4.62)$$

Instead of the magnitude n it is possible to introduce the average molecular weight of products of explosion $\bar{\mu} = 1/n$; then

$$D = \frac{k+1}{k}\sqrt{\frac{kRT_2}{\bar{\mu}}}. \qquad (4.62a)$$

From equations (4.62) and (4.62a) it follows that the speed of detonation other things being equal, should be proportional to the square root of the temperature of detonation T_2 and the number of gas moles per unit of weight n (or the reciprocal square root of the average molecular weight). For calculation of D the expression (4.62) and (4.62a) are inconvenient, since T_2 — the temperature of detonation enters in them, which is not equal to the temperature of instantaneous transformation with a constant volume $T = q/c_v$. Due to additional heating up during compression in the detonation wave $T_2 > q/c_v$.

For determination of the speed of detonation it is possible to conduct a relationship, in which will enter only the specific heat q and magnitude $k = c_p/c_v$. For this purpose we will introduce into the examination the enthalpy H, or thermal function, given by the relationship

$$H = c_pT.$$

For a theoretical gas

$$H=c_pT=\frac{k}{k-1}pv.$$

Inasmuch as the internal energy is

$$E=c_vT=\frac{1}{k-1}pv,$$

then

$$H=E+pv. \tag{4.63}$$

For difference of specific internal energies of two states according to the expression (4.52) we have

$$\varepsilon-\varepsilon_0=\frac{p+p_0}{2}(v_0-v).$$

Correspondingly for the difference of enthalpies, considering (4.63), we obtain

$$H-H_0=\frac{v+v_0}{2}(p-p_0). \tag{4.64}$$

The enthalpy of the initial state, taking into account the specific potential chemical energy of q, is separated during reaction in the form of heat, and is equal to

$$H_0=\frac{k}{k-1}p_0v_0+q.$$

The enthalpy of products of detonation (condition at point 2) is equal

$$H_2=\frac{k}{k-1}p_2v_2.$$

According to the expression (4.64) should be observed the equality

$$H_2-H_0=\frac{v_2+v_0}{2}(p_2-p_0)$$

or

$$\frac{k}{k-1}p_2v_2-\frac{k}{k-1}p_0v_0-q=\frac{v_2+v_0}{2}(p_2-p_0). \tag{4.65}$$

Let us note that in the case of real detonational processes the chemical potential energy q significantly exceeds the magnitude

$$\frac{k}{k-1}p_0v_0=c_pT_0.$$

Since

$$\frac{k}{k-1}p_0v_0\ll q$$

and simultaneously

$$\frac{k}{k-1}p_0v_0\ll\frac{k}{k-1}p_2v_2,$$

that in equation (4.65) the magnitude $k/k-1$ p_0v_0 can be disregarded, in exactly the same way it is possible to disregard the magnitude p_0, small is compared to p_2. Then

$$\frac{k}{k-1}p_2v_2-q=\frac{v_2+v_0}{2}p_2. \qquad (4.66)$$

Conducting a simple conversion and reduction in the expression (4.66), taking into account (4.61) we obtain

$$p_2v_0=2(k-1)q. \qquad (4.67)$$

Earlier we saw that

$$D^2=kv_0^2\frac{p_2}{v_2}=k\frac{v_0}{v_2}p_2v_0.$$

Replacing $v_0/v_2 = k + 1/k$ and $p_2v_0 = 2(k - 1)q$, we obtain

$$D^2=2(k^2-1)q,$$

or

$$D=\sqrt{2(k^2-1)q}. \qquad (4.68)$$

In formula (4.68) the speed of detonation is expressed as a function of only the specific heat of explosion q and the magnitude k. This expression is used significantly more conveniently than the formulas (4.62) or (4.62a). The specific heat of the explosion is a basic characteristic of an explosive. It is true exact calculation of the values k, taking into account the change of heat capacity depending on the temperature and pressure, is not a simple problem. It is necessary however, to consider that the magnitude $k = c_p/c_v$ for practically utilized explosives and gas mixtures is changed within small limits.

With temperatures characteristic for detonation k = 1.17, if the products of explosion consist wholly from triatomic molecules (CO_2, H_2O) and k = 1.28, if the products of explosion consist of diatomic molecules (CO, N_2 etc). Usually products of explosion constitute a mixture of triatomic and diatomic molecules, and the value k oscillates from 1.20 to 1.25. If in the products there are more diatomic molecules, then k = 1.25 (hexogene); if in the products there are more triatomic molecules, then k = 1.20 (nitroglycerine).

Let us give as an example the calculation of the speed of detonation of a gas mixture of the composition $2H_2 + O_2$. Let us note that if in formula (4.68) the value of specific energy is put in erg/g, then the value of the speed of detonation will be obtained in cm/sec. In order to obtain the value of the speed of detonation in m/sec, during substitution of q in usual thermal units (cal/g or kcal/kg) it is necessary to introduce a factor 64.6:

$$D = 64{,}6\sqrt{2(k^2-1)q}\ \text{m/sec} \qquad (4.68a)$$

Equation of the reaction

$$2H_2 + O_2 = 2H_2O + 115\ \text{kcal}$$

Hence per unit of weight

$$q = 3200\ \text{kcal/kg}$$

Take k = 1.17, then

$$D = 64{,}6\sqrt{2(1{,}17^2-1)3200} = 3150\ \text{m/sec}$$

Experimental determination of the speed of detonation gives a value of 2830 m/sec.

Divergence of the calculated and experimental value of the speed of detonation is easily explained. The fact is that during detonation of a hydrogen-oxygen mixture very high temperatures are developed, at which dissociation of water occurs by the equation

$$2H_2O \rightleftarrows 2H_2 + O_2$$

and even dissociation of hydrogen

$$H_2 \rightleftarrows H + H.$$

If one were to consider dissociation then the total equation of the reaction will have the form

$$2H_2 + O_2 = 1{,}54H_2O + 0{,}23O_2 + 0{,}33H_2 + 0{,}26H + 75{,}0 \text{ Kcal}.$$

This gives per unit of weight q = 2080 kilocalorie/kilogram.

It is necessary to consider not only the change of specific heat of the explosion, but also the change of k. Now the products of an explosion only by 2/3 consist of triatomic molecules therefore, we will take k = 1.21. Then

$D = 64{,}6\sqrt{2(1{,}21^2 - 1)2080} = 2840$ m/sec which practically coincides with the experimental value of 2830 m/sec.

Above, in Section 3, it was noted that an addition to a fulminate mixture of helium or additional quantity of hydrogen which appear as ballast in the energy relation, lowering the heat and temperature of detonation, does not decrease, but increases the speed of detonation. This circumstance completely is explained by theory. From the equation (4.62 or 4.62a) it is clear that the speed of detonation with this increases since the introduction of helium or excess hydrogen significantly lowers T_2, but simultaneously increases n (decreases μ), and also k.

As an example we will calculate the speed of detonation by the formula (4.68a) for a mixture of $2H_2 + O_2 + 4H_2$ without calculation of dissociation. The specific heat of explosion of the mixture is equal to ~2600 kcal/kg. In the products of the explosion 2/3 will constitute hydrogen, at the same time the temperature will be lower, which promotes an increase of k. In this case k must be taken not lower than 1.26. Then we will obtain

$$D = 64{,}8\sqrt{2(1{,}26^2 - 1)2600} = 3600 \text{ m/sec}$$

The calculated (without calculation of dissociation) value of the speed of detonation (3600 m/sec) turned out to be significantly higher than the calculated in this way speed of detonation of the fulminate mixture, not diluted by hydrogen (3150 m/sec). Calculation of dissociation should somewhat lower the speed of detonation, however, in a mixture with a surplus of hydrogen this lowering will be small dilution by hydrogen lowers the temperature and decreases therefore, the dissociation. As a result a speed of detonation near 3500 m/sec is obtained, i.e., significantly larger than in case of an undiluted mixture.

Thus, in certain conditions the change of composition and properties of products (increase of the value of k) can with a surplus compensate for the decrease of heat of the explosion. Apparently, therefore, for hexogene ($k = 1.25$) the speed of detonation is higher than for nitroglycerine, having a large heat of explosion, but smaller value of k, equal to 1.20.

It is necessary once again to note that the formula (4.68), by which the speed of detonation is a function of only the specific heat q and k, is accurate only for products of an explosion, obeying the equation of the state of a theoretical gas. In the formula the initial density of the detonating system does not enter. Meanwhile for explosives with those densities which are used in practice the speed of detonation depends on the initial density. This says that the equation of the state of theoretical gases useful for gas mixtures of small density, is inapplicable for condensed explosives. The given question will be considered below in greater detail.

Already it was noted that in certain cases the speed of detonation practically does not depend on the diameter of the charge the character of the shell and so forth. In other cases the dependence of the speed of detonation in such factors is very significant. The presence of such dependence indicates that in the given conditions (the diameter of the charge, shell and others) during the time of reaction essential losses in lateral directions and incomplete liberation of heat occurs. Therefore, the state of products of explosion will be described not by the adiabat of Hugoniot corresponding to full liberation of heat but by an intermediate adiabat. The transition of this adiabat should also be accomplished by a corresponding tangent, as a result the speed of detonation will be lowered.

We will now conduct certain important relationships for parameters of the detonational wave.

First of all we will obtain a connection of the speed of detonation D and the speed w_2 of the flow of products of explosion at the point of Jouguet. According to the expression (4.50)

$$w_2^2 = (p_2 - p_0)(v_0 - v_2) \approx p_2(v_0 - v_2).$$

Replacing in this expression v_2 the relation $(k/k+1)v_0$ and instructing that according to (4.67) $p_2 v_0 = 2(k-1)q$, we obtain

$$w_2^2 = 2\frac{k-1}{k+1}q = \frac{2(k^2-1)}{(k+1)^2}q. \qquad (4.69)$$

Comparing this expression with (4.68) we directly find,

$$w_2 = \frac{D}{k+1}. \qquad (4.70)$$

According to the expression (4.44a)

$$p = \rho_0 D w,$$

consequently,

$$p_2 = \frac{1}{k+1}\rho_0 D^2. \qquad (4.71)$$

We will remind (see p. 331) that on the front of a strong shock wave

$$w=\frac{2}{k+1}D$$

and

$$p_1=\frac{2}{k+1}\rho_0 D^2.$$

Thus, in an initial explosive, compressed by a shock wave, the pressure and speed of the substance is twice higher than the pressure and speed in products immediately after completion of a reaction.

Imagine a system, in which chemical transformation occurs immediately in all points. Such transformation by instantaneous explosion is called conditional. We designate by p' as the pressure developed during instantaneous explosion. For an instantaneous explosion disregarding the thermal part of initial internal energy we obtain

$$e_1=\frac{1}{k-1}p'v_0-q.$$

or

$$p'v_0=(k-1)q.$$

As we have seen above [(see (4.67))],

$$p_2v_0=2(k-1)q;$$

hence

$$p_2=2p' \text{ and } p_1=2p_2=4p',$$

i.e., pressure in a detonational wave (at the point of Jouguet) turns out to be twice higher than pressure during an instantaneous explosion, but the pressure on the front of the shock wave is four higher than the pressure of an instantaneous explosion.

The density during an instantaneous explosion obviously is equal to the density of the parent substance $\rho' = \rho_0$; in a detonational wave, as we have seen,

$$v_2 = \frac{k}{k+1} v_0$$

or

$$\rho_2 = \frac{k+1}{k} \rho_0.$$

In accordance with a large pressure in the detonational wave the energy of the unit of volume also increases as compared to the energy of the unit of volume during an instantaneous explosion. The increased values of pressure density and energy of the unit of volume of products of detonation at the point of Jouguet as compared to values of these magnitudes during instantaneous explosion are the result of movement of the substance in the front of the detonational wave the result of redistribution "pumping" of the substance and energy from back parts of the detonational wave to the head part. In the back part of the detonational wave corresponding parameters have a smaller value than during an instantaneous explosion.

We will stop again on the question about the zone of chemical reaction during detonation. The theoretical curve of the change of pressure in time in a detonational wave is shown in Fig. 4.59. In accordance with the above stated and in particular with conditions of transition from adiabat for an initial explosion to an adiabat for products (see Fig. 4.58) in moment of income of the shock wave the pressure in the parent substance p_0 by a rapid change is increased to the value p_1. After this reaction starts in the substance. By measure of the passage of the

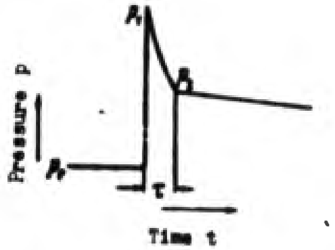

Fig. 4.59. Dependence of pressure on time in a detonational wave.

reaction and liberation of heat expansion of products of the explosion and lowering of pressure occurs. In an interval of time τ the reaction is completed and the pressure is lowered to value p_2 (pressure at the point of Jouguet). Subsequently the pressure continues to drop, but somewhat slower than in the zone of chemical reaction. In accordance with form of the curve p(t) the region of the reaction, characterized by heightened pressure is frequently called a "chemical peak." Let us note that at point 2 (see Fig. 4.58), as already noted, $c_2 = D - w_2$; in the zone of the chemical peak $c > D - w$, therefore, the energy release, occurring in this zone renders an influence on the leading front. Essentially the condition $c > D - w$ consititutes a condition of support of the front of the shock wave by the heat of the reaction which in the final result prevents damping and gives propagation with constant speed. The existence of a chemical peak is one of the most important theoretical conclusions of the hydrodynamic theory of detonation made and clearly formulated by Zel'dovich. This conclusion by far is not trivial. Really, without indications of the theory it would be difficult to imagine that the highest pressure is developed in the parent substance at the beginning of the reaction. For a gas detonation the presence of a chemical peak has been established experimentally. Regarding condensed explosives even more recently doubt has existed on whether the movement of curve p(t) (see Fig. 4.59) corresponds to the theoretical and in particular whether a chemical peak exists. Only recently the use of precise methods of experiment has made it possible to reveal a region of significantly heightened pressure in the head part of a detonational wave in the case of explosives. The curve of pressure — time on boundary of this region has sharp enough change. Thus the existence of a chemical peak similar to that predicted by theory has been proven. This circumstance again underlines the value of the hydrodynamic theory of detonation the importance and effectiveness of its basic conclusions.

The possibility of experimental detection of a chemical peak has an exclusively important value and makes it possible to estimate the time of reaction in the front of a detonational wave. This time is equal to the time from the moment of compression of the parent substance by shock wave to the moment of fracture of the pressure curve in the function of time corresponding to achievement of the point of Jouguet and transition from a reacting explosive to products of full transformation. From all possible appraisals of the time of reaction during detonation of the explosive, appraisal by duration of the chemical peak is at present the most reliable. Certain data on this question will be presented subsequently.

§ 12. The Theory of Detonation of Condensed Explosive Substances

1. The Dependence of Parameters of Detonation on the Density of the Explosive. Equation of the State of Products of the Explosion

In principle the hydrodynamic theory is applied also to the detonation of condensed explosives. However, calculation of the speed and other parameters of detonation in this case is hampered by the lack of a reliable equation of state for those extraordinarily dense gases which are formed during detonation. A second essential difficulty consists in the vague mechanism of excitation of chemical reaction in the front of the detonational wave, since heating up due to compression in the case of liquid and solid matters is relatively small even at very large pressures.

In examining the theory of detonation of gases we saw that the speed of detonation is simply determined by the heat of the explosion and the composition of its products:

$$D=\sqrt{2(k^2-1)q}.$$

This relationship is accurate only under the condition that the density of gaseous products is small and they obey the law of theoretical gases. For explosive gaseous systems at small initial pressures this condition is fulfilled and the speed of their detonation depends on the density only as much as the density renders an influence on the composition of products and heat of explosion.

For condensed explosives even at small initial densities gaseous products are so dense that their state can be described by an equation, just as for theoretical gases. There were attempts to use as an equation of the state of products of detonation a simplified Van der Waals equation

$$p(v-a)=RT, \tag{4.72}$$

which with success is applied in internal ballistics for calculation of the pressure during burning of powder in a closed volume. However, in the latter case maximum pressure did not exceed 4000-6000 atm (tech.). In the case of detonation equation (4.72) may be used only at very small densities of the explosive, which are considerably lower than met in practice. Densities of organic explosives in conditions of application are between 1 and 2 g/cm^3 with this pressures are attained, measured by hundreds of thousands of atmospheres. The density of gases during detonation obtains a larger density than the actual explosive and can exceed the density of liquid gases by more than 2 times. For these conditions, when the volume, located on one molecule, is comparable with its own volume, the equation (4.72), emanating from a constancy of volume, occupied by molecules, is knowingly inapplicable.

Thus, in the front of a detonational wave is realized an absolutely unique state, not accessible by other methods. Therefore, in order to determine an equation of the state for these conditions it was necessary to go by reverse means — to originate from experimental dependence of parameters of the detonational wave and on this base to conduct an accurate equation of the state for it. Landau and Stanyukovich, following this way, for the first time likened the state of products in the front of detonation to the state of a crystal grid of a solid. As is known, the energy of a solid has a double origin; it is composed of elastic energy conditioned by forces of the interaction between molecules, and from the thermal energy of oscillations of particles around their position of equilibrium.

Landau and Stanyukovich showed that in conditions of detonation it is possible, not accomplishing an essential error, to consider elastic energy and the elastic part of pressure as predominant.

Allowing in such a way that in products of an explosion with a density larger than the unit the pressure depends only on the density of the explosive and not on the temperature, it is possible by the experimental dependence $D = f(\rho_0)$ to establish an equation of the state $p = f(\rho)$.

From the expression (4.49), disregarding p_0, which is small as compared to p_2, we obtain*

$$p_2 = D^2 \frac{v_0 - v_2}{v_0^2}. \qquad (4.73)$$

Expressing the specific volume through corresponding densities, we find

$$p_2 = D^2 \frac{\rho_0(\rho_2 - \rho_0)}{\rho_2}. \qquad (4.73a)$$

In the equation (4.73a) the speed of detonation D is known from experience of the function of the initial of the explosive. Within limits of the densities 1-1.7 g/cm^3 especially approximately it is possible to consider that D is directly proportional to ** ρ_0:

$$D = A\rho_0. \qquad (4.74)$$

The constant A in coarse approximation constitutes for a typical individual explosive $4.5 \cdot 10^5$ cm^4/g sec that gives a speed of detonation of 4500 m/sec with $\rho_0 = 1$ g/cm^3 and 7200 m/sec with $\rho_0 = 1.6$ g/cm^3.

In the expression (4.73a) for p_2 enters also ρ_2 – the unknown density of products of explosion in the front of the detonation. Let us assume that this magnitude is proportional to the initial density of the explosive, i.e., $\rho_2 = h\rho_0$.

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*The index "0" is designated as the value of corresponding magnitudes for the parent substance, and index "2" – the same value in the front of the detonational wave, more exactly, at the point of contact (the point of Jouguet).

**In reality the speed of detonation somewhat weakly depends on the initial density; nonetheless usually the relationship of a direct ratio is used, which leads to more convenient for practical calculations by equations of gas dynamics.

Substituting in (4.73a) ρ_0 in place of D and ρ_2, we obtain

$$p_2 = A^2\rho_0^2\frac{\rho_0(h\rho_0-\rho_0)}{h\rho_0} = A^2\frac{h-1}{h}\rho_0^3. \qquad (4.75)$$

Designating $A^2\frac{h-1}{h} \equiv c$, it is possible to write

$$p_2 = c\rho_0^3. \qquad (4.75a)$$

Further from the expression (4.75) we have

$$p_2 = A^2\frac{h-1}{h^4}h^3\rho_0^3 = A^2\frac{h-1}{h^4}\rho_2^3, \qquad (4.76)$$

or

$$p_2 = B\rho_2^3, \qquad (4.76a)$$

where

$$B = A^2\frac{h-1}{h^4}.$$

Thus, from that experimentally determined fact that the speed of detonation is approximately proportional to the initial density of the explosive, it follows that the pressure in the front of detonation is proportional to the cube of the density of the explosive (and also to the cube of the density of products of the explosion).

The constant h can be determined from the expression for D finding its minimum since the point of tangency corresponds to a minimum from the possible speeds of detonation.

From (4.73a) and (4.76a) we find

$$D^2 = \frac{B\rho_2^4}{\rho_0(\rho_2-\rho_0)}. \qquad (4.77)$$

In order to find the value of ρ_2, at which D has a minimum (with given values of B and ρ_0), we differentiate D^2 by ρ_2 and compare with derivative of zero:

$$\frac{dD^2}{d\rho_2} = B\frac{\rho_0(\rho_2-\rho_0)4\rho_2^3-\rho_2^4\rho_0}{\rho_0^2(\rho_2-\rho_0)^2} = 0.$$

Since a denominator cannot be equal to infinity, then

$$\rho_0(\rho_2-\rho_0)\,4\rho_2^3-\rho_2^4\rho_0=0$$

or

$$3\rho_2=4\rho_0,$$

whence

$$\rho_2=\frac{4}{3}\rho_0, \qquad (4.78)$$

i.e.,

$$k=\frac{\rho_2}{\rho_0}=\frac{4}{3}.$$

For the pressure from (4.73a) we obtain

$$p_2={}^1/_4\rho_0D^2, \qquad (4.79)$$

and for the speed of gases behind the front on the basis of (4.47a) after replacement of v by 1/ρ we find

$$w=D\frac{\rho_2-\rho_0}{\rho_2}={}^1/_4D. \qquad (4.80)$$

Thus, during detonation of powerful explosives, as for example, tetryl (D = 7200 m/sec, density 1.6 g/cm^3) pressure in the front of the detonational wave attains 200,000 kg/cm^2, density of the products of the explosion is equal to 2.13 g/cm^3 and the speed of gases is 1800 m/sec. The equation of the state of products of the explosion of such an explosive according to (4.76a) has the form

$$p_2=20\,000\rho_2^3, \qquad (4.81)$$

or

$$p_2v_2^3=20\,000, \qquad (4.81a)$$

where p_2 is expressed in kg/cm^2, ρ_2 in g/cm^3 and v_2 in cm^3/g.

A more exact calculation, considering the thermal component of the pressure of the explosion, does not lead to an essential change of the equation of the state with which it is also necessary to use during calculations not forgetting its approximate character, and also the fact that in reality part of the pressure (almost 1/3) is of thermal origin and that the equation is applied only with a density ρ_0, greater than 1-1.3 g/cm^3.

Recently an experimental method was published on the measurement of pressure in a detonational wave, based on the basic relationship (4.44) for shock and detonational waves: $p = \rho_0 Dw$. In spite of the indirect character of determination, the method is reliable. According to the data given in the literature this method is applied to explosives of great density, with a great speed of detonation. During explosion of such explosives the pressures are especially great and the possibility of their measurement is most valuable.

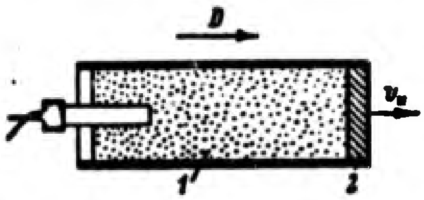

Fig. 4.60. System of experimental determination of the pressure of detonation. 1) charge of explosive; 2) metallic plate. [Н = 1 = initial]

Let us give a short description of the essence of the method. Figure 4.60 shows the charge of an explosive, by which detonation spreads. To the right end of the charge a thin metallic plate is densely pressed. As a result of the influence of the detonational wave a shock wave will start to spread in the plate. When the shock wave in metal attains the right (free) surface of the plate, this surface starts to move an initial speed of v_1, which is measured exactly. For metals the relationship $w_m = (v_1/2)$ is well fulfilled. Thus measuring the <u>initial</u> speed v_1 of the movement of the surface, we define w_m as the speed of flow of the substance in the front of the shock wave in metal of the plate. The determination of v_1 should be done on a small base (time of measurement should be less than double the time of passage of the shock wave on the plate). The magnitude of D_m was further determined as the speed of the shock wave in the metal. The value of D_m may be calculated, if the connection of D_m and w_m is known (equation of the dynamic adiabat of a metal), or is measured directly. Determining w_m, D_m and knowing the initial density of the metal ρ_{0m}, it is possible to calculate the pressure of a shock wave in metal,

$$p_м = \rho_{0м} D_м w_м. \qquad [м = m = metal]$$

In general case p_m is not equal to p_d – the pressure of detonation at the point of Jouguet (i.e., at the point of completion of chemical transformation) in a freely spreading detonational wave without reflection from the plate. The relation of pressures p_0/p_m depends on the relationship of the magnitude of $\rho_0 D$ (here ρ_0 is the density of the explosive D is the speed of detonation) and $\rho_{0m} D_m$ (product ρD is called acoustic rigidity).

If $\rho_{0м} D_м > \rho_0 D$, then $p_м > p_д$. $\qquad$ [д = d = detonational]

If $\rho_{0м} D_м < \rho_0 D$, then $p_м < p_д$.

The simple connection between p_d and p_m is given by the approximate formula

$$p_д = \frac{p_м}{2}\left(1 + \frac{\rho_0 D}{\rho_{0м} D_м}\right).$$

Judging by the source material, for plates usually aluminum is used as material, for which the above mentioned formula gives sufficiently good results; the thickness of the plates for powerful explosives is usually in the order of 1-2 mm.

In the literature are given the results of the measurement of pressures of detonation (at the point of Jouguet) of several explosives.

We will give corresponding data and compare it with the theoretical values, calculated by the formula (4.79). For hexogene (ρ_0 = 1.785 g/cm^3) at a measured pressure of $338 \cdot 10^3$ atm (tech.);

calculated is $346 \cdot 10^3$ atm (tech.). For trotyl ($\rho_0 = 1.64$ g/cm^3) the measured pressure is $189 \cdot 10^3$ atm (tech.); calculated is $200 \cdot 10^3$ atm (tech.).

If one were to consider the approximate character of the calculated formula, then one should consent to recognize as fully satisfactory. The obtained experimental values can be used for more precise definition of theoretical calculation.

Using very thin plates (several tenths of a millimeter) it is possible to fix a heightened pressure in the zone of chemical transformation. Conducting a series of experiments with plates of various thickness a complete idea about the width of zone of the chemical peak and change of pressure in it can be obtained.

Thus, the presented method gives experimental proof of the presence of a chemical peak, and also the possibility of the most reliable appraisal of the time of reaction in the front of the detonational wave (by a break of the curve of pressure as a function of time) for powerful full value-detonating explosives with a very great speed of chemical transformation.

From the above-stated fundamental essence of the method it follows that very high requirements must be presented to measuring equipment: it is necessary to measure with great accuracy the initial speeds of the surface of the plate on minute sections (bases) up to tenths of fractions of a millimeter (and also in certain cases the speed of propagation of shock waves — also on small bases). The existing possibilities and, in particular, the use of cathode oscillographs with large resolution in time completely satisfy these requirements.

2. Mechanism of Excitation and Development of Reaction During Detonation

During ordinary conditions in practice of explosion the speed of chemical transformation is sufficiently great so that all explosives succeeded to react in the detonational wave (in an interval from the front boundary of the front to the point of Jouguet). In these conditions the heat of reaction separates out sufficiently fast, in order to support propagation of the shock wave, determining the speed of detonation. The speed of detonation in such a case is not limited by the speed of chemical transformation and lately should not be calculated as we have done up to now. However, this is by far not always so. We saw that in a number of conditions for instance with diameters less limiting the possibility and speed of detonation essentially depend on factors, affecting the flow of the chemical transformation; from the diameter of charge its shell dimensions of particles, presence of inert impurities, etc.

In order to grasp the influence of these and analogous factors, one should consider the chemical-kinetic side of the phenomenon of detonation. It is necessary to clarify how a reaction in the front of the shock wave is evoked as it is developed and reaches or does not reach the end.

Excitation of reaction

The passage of a shock wave along an explosive is accompanied by a sharp increase of pressure in it. It would have been possible to assume that this compression is directly the cause of a fast flowing reaction but against such an assumption there is talk of the results of research of the influence of very large pressures (several tens of thousands of atmospheres) on thermal disintegration of an explosive, which did not reveal significant measurement of speed of reaction.

Experiments of Bridgman determined that the compression of an explosive even to 100,000 atm (tech.) does not lead to an explosion.

In connection with the lack of experimental data talking in favor of direct excitation of chemical reaction by compression of the explosive in the front of the shock wave* at present it is considered that excitation of the reaction is thermal i.e., that the temperature obtainable during compression of the explosive is sufficiently high, in order to evoke a rapid chemical reaction.

A specific mechanism for heating up provoking a chemical reaction may be different.

In liquid explosives, not containing gas bubbles or in homogeneous solid explosives detonating with high speeds compression by shock wave in the front of the detonation apparently may cause sufficient heating up for excitation of a fast reaction. Such a mechanism of excitation one should consider possible during speeds of detonation of the order of 6000-8000 m/sec. For nitroglycerine for instance by calculation approximately due to inaccurate knowledge of the equation of the state of the explosive at high pressures the temperature in the front of shock wave is not less than 1000°C. At low (~2000 m/sec) and average speeds of detonation the increase of temperature at the expense of compression of the condensed substance is not considerable (in the order of tens of degrees) and cannot by

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*It is necessary however, to note that the pressures experimentally studied with respect to the influence of them on the speed of chemical reactions nevertheless are considerably lower than those, which take place during detonation. Besides this in light of the above considered considerations mainly about the elastic origin of pressure in the front of the detonation wave it remains vague whether the temperature attained during compression is sufficient in itself to evoke an extremely rapid reaction. During an appraisal of the temperature it follows, indeed, to consider the share of elastic energy significantly less than the share of elastic pressure.

itself ensure the needed speed for stationary detonation of chemical transformation.

Recently Cook advanced a new hypothesis about the mechanism of excitation of a chemical reaction during detonation. Proceeding from the experimentally fixed fact that the passage of a shock wave on a substance evokes its strong ionization Cook concludes that thermal conduction should increase correspondingly, where to such a degree that the speed of propagation of heat from the chemical reaction can significantly exceed the speed of the shock wave. Thus, the basic role of the shock wave leads to that which, ionizing the substance, it paves the way for propagation of the thermal wave, which heating the explosive, evokes fast chemical transformation.

The basic argument in favor of this point of view are experiments on transmission of detonation through a plate of inert material. High-speed photography shows that entry of the shock wave in a passive charge does not lead immediately to excitation of its detonation and the latter appears only at a certain significant distance and usually spreads from the point of appearance not only forward, but also backwards.

Delay of the appearance of detonation is explained by Cook by the fact that through the inert plate passes basically only a shock, and not a thermal wave. A shock wave itself cannot evoke a rapid chemical reaction and the latter appears in this case after a certain period of development in the moment, when the shock wave already succeeded to pass forward. When a thermal wave (in nitromethane the speed of it according to Cook attains 35,000 m/sec) overtakes the shock wave, detonation appears accompanied as usual, by an intense glow, recorded by photography.

Figure 4.61 shows consecutive photographs (in reflected light) of the transmission of detonation through a barrier of organic glass with total thickness of 6.3 cm. Frames 1-5 show propagation of the shock wave in the glass, in frame 7 the wave reaches the surface of the passive charge. Frames 9-15 show propagation of the shock wave in the passive charge not accompanied by a reaction. This wave is conspicuous by change of color, caused by the appearing roughness of the surface of the charge distinctly noticeable on the original

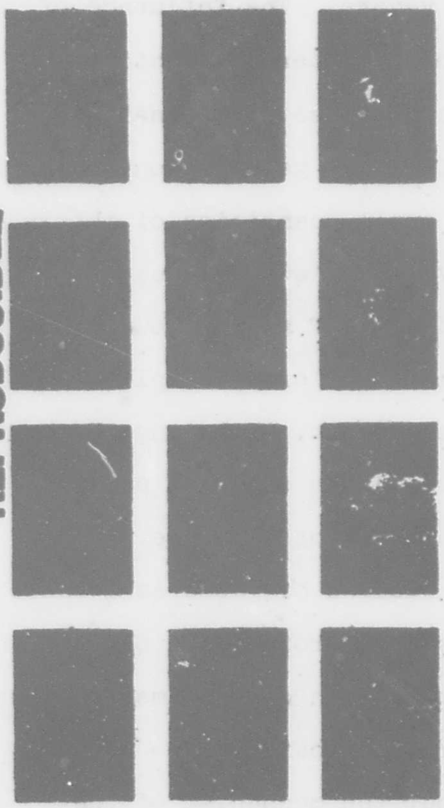

Fig. 4.61. Appearance and development of detonation during transmission of it through an inert barrier.

colored photography. Between frames 15 and 17 detonation starts spreading as one may see to frames 17 and 19 in both directions.

It is necessary to indicate that these observations comprising the experimental basis of the hypothesis of Cook, can also obtain another interpretation.

Along with a homogeneous mechanism of heating up another is also possible, when the reaction starts in separate points of the explosive, where local heating up appeared, similarly as this occurs during excitation of an explosion by a mechanical blow (see Chapter V).

Local heating up can be formed by various ways.

If an explosive is mechanically nonuniform then during passage of a shock wave particles or layers of it go into movement with various speeds and friction appears between them. Furthermore, with mechanical heterogeneity the explosive is nonuniform and heating up is evoked by the shock wave. The irregularity of heating up favors the appearance of hearths of reaction in sections, where the temperature turned out to be high.

Mechanical heterogeneity of an explosive can appear from different causes for instance, due to the presence in the explosive of little inclusions (bubbles) of gases or vapors. The influence of bubbles can promote an extraordinarily high temperature obtainable during their compression. A significant increase of detonational ability is observed also with introduction into gelatins on the basis of nitroglycerine and nitrocellulose of small quantities of thinly crushed inert heavy impurities. Finally, local surface heating up can also appear due to penetration of streams of hot gaseous products of the explosion in the pores between particles of the explosive. It is possible to imagine also a combined mechanism, including the appearance of burning in bubbles and propagation of it by pores, which are forming as a result of an increase of pressure in the hearth of the reaction. Compression of bubbles of gases as a cause of the appearance of local heating up is very probable in the case of gelatin, containing bubbles of air. Penetration of streams of gases in pores can occur in the case of powdered explosives.

In connection with the question about the mechanism of the appearance of local heating up during detonation one should remember the strong dependence of the detonational ability of solids on the physico-mechanical structure of charge. The more homogeneity of the explosive, the more difficult it detonates. Large crystal and especially poured charges detonate much more difficultly than fine-crystalline. Apparently in spite of extraordinarily large pressures with which substance is subjected during passage of a detonational wave splitting of particles does not succeed to occur sufficiently fast and a chemical reaction appears and is developed in the first place on that surface, which preexists in the charge.

The physico-mechanical structure of the charge determines not only the possibility of propagation, but also the ease of appearance of detonation. One of the probable factors which determines this influence are the dimensions of bubbles of gas heating up of which leads to formation of hearths of reaction.

In general it is possible to imagine certain optimum dimensions of bubbles. With large bubbles a higher temperature is attained, but the specific surface on which burning also appears, is small. If the bubbles are small then heating up of them is less because of the large heat withdrawal in the condensed phase. If it, however, is still sufficient for ignition of the explosives, then the burning appearing on the whole from a large specific surface is developed more intensely. For various explosives with their different inflammability and dependence of the burning rate an pressure an optimum dimension of bubbles may be distinguished.

Which gas is included in the bubbles has the exact same role. Thus replacement of air in powdered trotyl with a gas with a smaller heat capacity (argon) led to an increase of the speed of detonation from 1380 to 1580 m/sec. The increase of the speed of detonation was observed also in the case of a mixture of ammonium nitrate with aluminum. These facts confirm the assumption about the fact that during propagation of detonation not only heterogeneity created by gas pockets plays a role, but also heating up by their shock wave. The more heating up naturally the larger the magnitude of k (equal to c_p/c_v) of the corresponding gas. The compression of bubbles of gas also occurs during detonation with great speed; the temperature obtainable in them during compression can exceed 10,000°C but in this case even condensed phase may be strongly heated up by compression and ignition of the explosive can occur in mass, as well as on the surface of the gas section – a solid explosive (or liquid). With low

(~2000 m/sec) and average speeds of detonation the increase of temperature in condensed phase is insignificant, when an increase of temperature in gas bubbles is still very great and with usual conditions may cause extremely rapid ignition on the surface of the condensed and gas phases.

An increase of the initial pressure in the bubbles should decrease the temperature of local heating up and thus hamper the appearance and propagation of detonation. Actually experiments showed that an increase of pressure on powdered explosive lowers the low speed of detonation and can even lead to its ceasing.

Extraordinarily high temperatures obtainable during compression of gases by shock wave are convincingly confirmed by results of experiments of Mürauer, who established that the intensity of the glow (so-called flame of explosion) during explosion of a charge of explosives in encirclement of certain gases may be very great. Along with this it strongly depends on, what gas surrounds the explosive. Monatomic gases for which k is great; give a much more intense glow than gases the molecule of which consists of many atoms.

Latest research has established that during detonation of powdered explosives not only are external light effects conditioned by the fast compression of the atmosphere surrounding the explosive, but that a large part of the light from the explosive is also radiated by compressed gas pockets.

It turned out that the glow during explosion of powdered explosives depends on the nature of the gas, filling the intervals between the particles. In Fig. 4.62 is given a photograph of detonation of a charge of tetranitrate, in which air was replaced with butane in one part of the charge and argon in a part of the charge from the other end; in the middle part of the charge air remained. The intensity of the glow was the greatest in the section with argon and least with butane. And it should be thusly, inasmuch as adiabatic compression of argon gives a much higher temperature than compression to the same pressure of the butane, which has a large heat capacity;

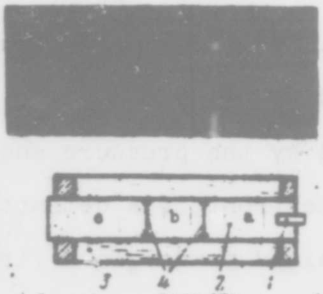

Fig. 4.62. Detonation of a charge of granulated tetranitrate, composed of three parts. In part a) intervals between particles are filled with butane, in part b) with air, in part c) with argon. The photograph was done through a narrow slot. 1 — detonator, 2 — tetranitrate, 3 — water jacket, 4 — membrane.

air occupies the intermediate position.

It was also shown that intense radiation is obtained from granulated table salt if one were to place it in larger form in a very dense plastic explosive and explode this laminated charge in water (Fig. 4.63). An explosive, containing almost no air, emits very little light and only leaves a weak trace on the photographic film (the glow of air, adjoining the explosive from without was removed by encirclement of the charge by water). This proves that gas pockets even if they are not in the explosive, but in an inert powder, are strongly heated during passage of a shock wave.

Fig. 4.63. Photograph of a laminated charge showing an intense glow in the zones of location of a salt.

Development of the reactions

Whichever of the considered mechanisms was called a chemical reaction in the front of the detonation its further development apparently always occurs nonuniformly, which is very essential for understanding the influence of different factors on the flow of the process.

The micro-heterogeneous flow of the reaction which appears as a means of local heating up is quite natural. Starting on the surface of the particle the reaction spreads in its depth in the form of unique rapid burning with a speed, determined by the pressure and temperature of the gases. This process in the front of a detonational wave suggests burning of a charge of fine-grained powder in a firing weapon with the only difference that the pressure during detonation is several orders greater. To calculate the time of burning of a particle of an explosive is difficult first because of the unique character of burning. With a small thickness of particles there is a relatively great time of non-stationary conditions during ignition and at the end of burning of the particle. Secondly the dependence of the burning rate on pressure is determined only in a narrow interval of the latter – at relatively low pressures. If, nevertheless, this data is extrapolated on a pressure of the order to 100,000 atm (tech.) then burn-up time of a particle with dimensions of several of a millimeter should be sufficiently small (of the order of one microsecond) so that the particle succeeded to burn in the detonational wave.

As another possibility, besides burning of particles of explosives from the surface it is possible to consider a relatively slower reaction in the *mass* of the particle. However, so that the role of such a reaction is essential the temperature of the particle should be increased to a level, at which reaction will pass with very great speed. A sufficient increase of the temperature of the particle in principle should be evoked by compression in the shock wave; if the intensity of the latter is insufficient for that, then the only other possible way of increasing the temperature of the particle is in its heating up by means of thermal conduction. Calculation shows however, that an increase of the temperature inside a particle with a diameter of a total of 0.1 mm, being in hot gases, becomes significant not earlier than in 10^{-4} sec. In reality the times of the reaction are much less. Thus, with experimental data on the appearance and development of a reaction during detonation of an explosive only the mechanism of the appearance of reaction on the surfaces and propagation of it in the depth of the particles by means of fast burning coincides with moderate and low speeds.

It is necessary to add that during detonation of a powdered explosive a particle does not have to burn completely. The following experiment can serve as an illustration.

A charge with a diameter of 50 mm of small rectangular flakes of smokeless powder (1 × 1 × 0.323 mm) was detonated with a density of 0.77 g/cm^3, where the speed of detonation constituted 2300 m/sec, which was a significantly lower speed than calculated by the hydrodynamic theory. During the explosion residue of the incompleteness of burnt grains was observed. Some of them were measured, and the average thickness of them turned out to be equal to 0.271 mm instead of 0.323 mm. Weighing showed that during detonation only about 30% of the explosive reacted.

The idea about the appearance of the reaction during detonation as a result of heating up of gas pockets and subsequent its flow as burning to their surface is difficult to apply to the detonation with high speed observed in charges of nitrogelatin of small diameter initiated by powerful detonators. Thus it is difficult to apply them for an explanation of the very fast reaction in liquid and certain solid explosives, where the possible surface of gas pockets, and consequently also burning, cannot be much larger than the surface of the front of the shock wave.

In these cases one should allow that the reaction is excited in the mass of the explosive as a result of its heating up evoked by compression by the shock wave. How this reaction is further developed is not fully clear. It is possible to imagine its homogeneous development. It is more probable however, that in the considered case the development of the reaction has a local character. After heating up even if it was uniform by the entire mass of the explosive, not all molecules react simultaneously, and at first only those, the energy of which exceeds the activation energy. As a result of the exothermic nature of the reaction in place of its appearance the temperature is increased still further, a hearth of the reaction will be formed in the form of a bubble of extraordinarily heated up gases from which burning spreads to all sides. It is possible to imagine the initial stage of formation of the hearth of the reaction as a chain process, which is possible during those very high temperatures of an explosive, which are attained by compression by its shock wave.

Thus, apparently in this case as well, the reaction evoked by a shock wave flows in the explosive nonuniformly, and the main distinction consists in the mechanism of the appearance of the hearth of the reaction; here — as a result of homogeneous heating up of the condensed phase, and in the above considered case — as a result of heating up of the bubbles. As can be seen heterogeneity of the flow of the reaction is possible also with "homogeneous" excitation of it.

When an explosive is able to detonate with two different speeds it is natural to allow that the small speed of detonation is caused by excitation of the reaction in bubbles, and the large — by homogeneous initiation. The detonation evoked with a small speed can spontaneously cross into detonation with great speed. This transition can occur both in the form of relatively slow acceleration as well as a sudden change of speed (Fig. 4.64).

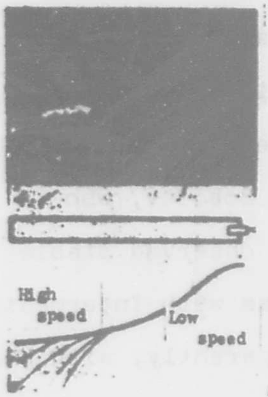

Fig. 4.64. Photograph on photoregister of transition of detonation with small speed to detonation with great speed (6000 m/sec) for a nitroglycerine explosive.

During excitation of slow detonation the pressure in the front of the shock wave is small and the reaction frequently does not reach the end; it starts in compressed bubbles and spreads by means of the surface burning of particles with subsequent secondary reactions of products of disintegration in the gas phase. With an increase of pressure and speed of detonation the particles of an explosive are subjected to compression with a corresponding increase of their temperature. This increase of temperature leads to an additional increase of the burning rate. With a definite pressure compression of particles becomes so great that reaction in volume starts to play a role. It is possible that in certain conditions the reaction appears in parallels on the surface of the particles and inside them. With a further increase of pressure the inner-particle appearance of the reaction obtains the predominant role. In this case the presence of gas bubbles cannot essentially affect stationary propagation of the process although it is able in spite of this to render a significant influence on its appearance (sensitivity of the explosive).

The considered presentations are applied not only to chemically uniform explosives, but also to mixtures, consisting of components of various reactivity, for instance from detonating explosives, oxidizers and nonexplosive fuels. In this case the surface burning of particles of different components of the given layer of the explosive occurs with various speed and therefore nonsimultaneously.

Means of diffusion and micro-mixing of gases, obtained during disintegration of separate components are mixed and react.

A very convincing illustration of the possibility of two different mechanisms of detonation for one and the same explosive are given in the described earlier experiments of Bobolev, who for ammatol 50/50 with a small diameter of charge observed stable detonation with small and large densities whereas with intermediate values of density, detonation did not spread. Apparently, with small densities a "bubble" occured (or flowing) appearance of detonation with large densities, detonation appeared homogeneously in compressed explosivies. Confirmation of this explanation is the fact that in the region of small densities dependences were fulfilled (influence of density on the critical diameter) typical for detonation of mixtures with large densities — dependences, which are peculiar to individual powerful explosives. In the region of intermediate densities the bubble (or flowing) mechanism no longer is in a state to ensure a rapid reaction and a homogeneous still cannot do this; as a result detonation turns out to be impossible. This explanation does not contradict the possibility of detonation with intermediate densities in conditions of large diameters of the charge when for stable propagation of detonation even those lowered speeds of chemical transformations are sufficient which are ensured with these densities by separate mechanisms or their joint action.

The mechanism of influence of different factors on the appearance and propagation of detonation. Khariton principle

As we have seen, a constant speed of detonation is observed only in the case when the diameter of a cylindrical charge of an explosive exceeds a certain limit, characteristic for the given substance. With a decrease of the diameter of the charge, starting from the limit the speed of detonation decreases and at a certain minimum critical diameter, detonation does not spread. Khariton, establishing the existence of a critical diameter, made from tnis fact fundamental conclusions of the fundamental value. The existence of a critical diameter according to Khariton is connected with the fact that the speed of chemical transformation during detonation is not infinite, but has definite finite values.

During detonation a shock wave goes along the explosive. Compression leads by some mechanism or another to excitation of a chemical reaction in the explosive. Simultaneously the high pressure in the compressed substance evokes radial expansion of it, leading to a drop of pressure to scattering of the reactant.

As a rule, not only gaseous products of incomplete reaction, but also particles of a condensed explosive, which have not been burnt, are subject to scattering. Pressure promotes flow of chemical transformation, expansion prevents it.

The maximum possible pressure is determined by the potential energy of the explosive, its composition and density and is definite for every substance by magnitude. The flow of scattering depends on the characteristics of the charge, in the first place on its radius since a drop of pressure as a result of expansion starts from the periphery and spreads from it to the axis of the charge. This drop of pressure in other words a wave of rarefaction spreads with a definite speed equal to the speed of sound in the medium in which propagation occurs. Time θ during which a wave of rarefaction attains axis of the charge, is equal to the relation $\frac{d/2}{c}$ – the radius of the charge of speed of the wave of rarefaction is equal to the speed of sound. If this time is greater than the time necessary for completion of chemical transformation then scattering cannot be reflected on the flow of detonation in the axial part of the charge; in this case, detonation spreads with maximum speed peculiar to the given explosive. If the wave of rarefaction succeeds in reaching the axis of the charge earlier than the reaction is completed, then it to larger or smaller measure decreases the fullness of transformation and lowers the maximum pressure obtainable during detonation. When this lowering is small and the pressure in the reacting layer is sufficient, to compress the following layer of the explosive and to evoke in it a rapid reaction then detonation spreads stably, but with a speed, smaller than the maximum.

If lowering of the pressure, evoked by the wave of rarefaction, is great then the delay of chemical transformation can become so large that propagation of it will be stopped. The diameter of charge during the transition through which this occurs also constitutes the critical diameter of detonation of the given explosive.

The time necessary for completion of the reaction, is connected with properties of the explosive and its state. This time can be changed within very wide limits and it basically determines the detonational ability of the substance. Thus for instance, the time of reaction of lead azide other things being equal, in tens of times less than hexogene. In turn, the time of reaction of hexogene is approximately in 300 times less than ammonium nitrate.

The time of reaction naturally depends not only on the chemical nature of the explosive, but also on its physical structure in particular, on the dimensions of the particles, which constitute it or were formed by the action of the shock wave. The smaller these particles, the faster their combustion passes to the front of the detonational wave.

The time of scattering is defined as the pressure, developed in the front of the detonational wave, as well as the diameter of the charge, and also the mass and durability of the shell. Time of scattering minutely differs in different substances by comparatively small distinctions in the speed of detonation. One may assume that for various explosives (with a given diameter of charge) it differs only 2-3 times.

The less the diameter of the charge, mass and durability of shell, the less time of scattering as well. From these considerations it follows that the possibility of detonation is determined not by any absolute value of the speed of transformation or time of its flow. It depends on the relationship between this time and the time, given for flow of the reaction which is limited by scattering of the substance.

It follows from this in particular, that owes any substance or mixture should detonate, in which the mechanical and thermal action of products of chemical transformation accelerate it, whatever the mechanism and duration of the actual transformation were. In other words any system capable of exothermic transformation in principle, is explosionable. With ~~the~~ this more duration of transformation the bigger should the diameter of the charge be at which stationary detonation can take place. Many substances and mixtures, which in usual conditions are not considered explosive can become explosive if dimensions of the charge are sufficiently great and sufficiently strong initiation is used.

The fact that chemical transformation during detonation of an explosive, also including individual chemical compounds passes in a noticeable time by means of gradual gas forming, one may see first of all from experiments, in which the charge of the explosive detonated in an encirclement of finely pulverized inert material. With such experiments not only significant quantities of gaseous products of incomplete transformation were obtained, but also a lot of undecomposed condensed explosive, which can be explained by rapid cooling and lowering of pressure of gases of the explosion during their contact with the inert material. The finer components of the mixture are crushed (if a multicomponent mixture is detonated) the more complete flow of transformation other things being equal.

A decrease of the critical diameter of the charge of individual powerful explosives with an increase of density should be explained by the fact that the growth of pressure, which the increase of density leads to, accelerates the flow of reactions in the detonational wave to a larger degree than it accelerates scattering.

In the case of mixtures as we have seen an increase of density leads to an increase of the critical diameter. This should be explained by the delay of development of the chemical reaction between products of gas forming of components with large densities. Such an influence is conditioned by the difficulty of penetration of gases in narrow pores, and also by the delay of mixing products of the reaction at heightened pressures obtained with large densities. It is also possible that in case of mixtures (or weak individual explosives) the optimum dimension of bubbles is greater than in the case of powerful individual explosives, and with a growth of density the dimension of bubbles of the gas decreases.

A massive shell favors detonation; this appears in particular in lowering the critical diameter and is explained by the fact that the shell hampers and delays scattering; with this the time of transformation is not changed or even decreases. In a very durable, not bursting during detonation shell, scattering is practically smoothed and the critical diameter is sharply lowered. The fact that it nevertheless exists is explained by losses of heat in heating up the shell which start to show with very small diameters. Cooling of reacting explosives brakes its transformation.

Theory of Khariton makes it possible also to consider the influence of inert impurities on the possibility and speed of detonation. Inert impurities usually decrease the speed of detonation, and with a large content its propagation impossible. The main role here is again played by that circumstance, whether particles of inert impurities simply scatter or will they more or less significantly participate in the exchange by energy with the reacting explosive and products of its disintegration. In the last case, the presence of inert impurities will essentially hamper detonation of the explosive; in the first case — it will appear much weaker. An important factors are the dimensions of particles of the explosive and impurity; the smaller the particle i.e., the more surface, on which the release of energy by the explosive to particles of the impurity occurs, the greater it will absorb energy and the stronger will be its influence. The chemical reaction rate of an explosive, diluted with inert impurities also plays a role. The greater the speed, the less will be the relative influence of the inert impurity.

However, inert impurities can not only hamper propagation of detonation, but also facilitate it. This is observed in the case, when a particle of an explosive is comparatively large and the presence of an impurity increases the average density of the powdered substance. With large particles the specific surface of heat exchange of them with the inert impurity is small and an increase of density increases the inertial resistance to scattering. In these conditions the action "of heavy" impurities to a known degree are analogous to the action of the outer shell.

The principle of Khariton makes it possible to give a tentative appraisal of the time of reaction in a detonational wave proceeding from experimentally easily definable magnitude of the critical diameter. For critical conditions the time of scattering θ is equal to the time of the reaction τ. The time of scattering is approximately equal to the time of passage of the sonic wave to the axis of the charge, i.e.,

$$\theta \approx \frac{d_\text{к}}{2c}. \qquad [\text{К} = c = \text{critical}]$$

From (4.60) it follows that c = D-w, and according to the formula (4.80)

$$w = {}^1/_4 D, \tag{4.82}$$

therefore

$$c = \frac{3}{4} D$$

and

$$\tau = \theta = {}^2/_3 \frac{d_\text{к}}{D}. \tag{4.83}$$

For powdered trotyl with a density of one g/cm^3 the critical diameter is equal to 0.8 cm, and speed of detonation is 5000 m/sec. Hence

$$\tau = {}^2/_3 \frac{0.8}{5 \cdot 10^5} \approx 10^{-6} \text{sec} \approx 1\ \mu\text{sec}.$$

By similar calculation lead azide we obtain that τ lies in limits from $3\cdot10^{-3}$ to $6\cdot10^{-3}$ microseconds. For hexogene and ammonium nitrate the time of reaction constitutes respectively 0.1 and 30 microseconds. Thus, the time of reaction in a detonational wave for lead azide is several thousand times less than the time of reaction of ammonium nitrate which, however, can be seen directly from a comparison of critical diameters (distinction in speeds of detonations are small).

As was shown (p.360) for charges of great density there is a more direct experimental method of appraisal of the time of the reaction. The dependence of the pressure on time in the detonational wave has a sharp break at the point of Jouguet i.e., at the point of completion of the chemical reaction. The times of reactions obtained proceeding from this dependence turn out to be many times less than those calculated from the principle of Khariton. This distinction is explained by the following.

During detonation of charges of large diameter far from critical conditions the pressure in the front is great and the speed of the reaction is accordingly great. With detonation near critical diameter the magnitude of loss, lower pressure, correspond to the lower speed of reaction and greater time of its flow. In other words with a diameter, equal to the critical i.e., in case of detonation of a charge, hardly able to explode the time of reaction being on the edge of damping, is significantly larger than with a large diameter when pressure from scattering does not drop and the reaction flows with maximum speed.

The hydrodynamic theory of detonation as already shown in its general positions is applied also to the case of detonation of condensed explosives. How does the phenomenon of scattering accompanying the passage of detonation, reflect on the mechanism, which the hydrodynamic theory considers? The hydrodynamic theory assumes that on front edge of the detonation front there is a shock wave spreading with the speed of detonation, but with a much greater pressure and that this corresponds to the point of tangency on the Hugoniot curve. After compression by one or another means of provoking chemical transformation of the explosive, simultaneously with this transformation expansion occurs along the straight line 1-2-0 (see Fig. 4.58), shifting the parameters of the explosive from a state which correspond to the initial substance, in a condition corresponding to products of the reaction.

Quantitative theory shows that in all states lying between point 1 and the point of tangency 2 the speed of propagation of the state is less than the total speed of sound corresponding to the given intermediate state of reaction and speed of the substance w. Therefore, any disturbance appearing at this stage of expansion and spreading to the reacting moving substance with the speed of sound* overtakes the front of the shock wave and thus influences the pressure in it and the speed of its propagation. At the point of contact the speed of detonation is equal to the sum of the speed of sound and speed of the movement of the medium; below the point of tangency the speed of propagation of the state is less than the sum of the speeds of sound and the medium. Therefore, no changes occurring behind the front of detonation after transition of the

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*That is spreading in a motionless system of coordinates with a total speed, equal to the sum of the speed of the substance and the speed of propagation of sound in it.

substance to the state, meeting point 2 can overtake the front of the wave and be reflected on its propagation.

Thus if a reaction is completed to achievement the point of tangency then the subsequent inevitable expansion of gaseous products of the reaction cannot affect the speed of propagation the magnitude of which is determined by coordinates of the point of tangency. With diameters of a charge larger than the limit, this condition is fulfilled. If the diameter of the charge is less than the limit then during the time of the reaction because of scattering an additional expansion occurs and pressure at the point of contact will be less than it was with large diameters of a charge with complete energy release. Accordingly the speed of propagation will be less. Lowering of pressure at the expense of scattering is negatively reflected on passage of the reaction incompleteness of it is increased which in turn brakes the reaction further. As a result with a critical diameter of the charge, the compression of the substance in the caused detonation on the shock wave turns out to be insufficient for excitation rapid chemical reaction and detonation stops.

In the case of an explosive, detonating by the "gas" (homogeneous) mechanism, ceasing of detonation is observed at comparatively high speeds of detonation since for heating up of condensed explosives large pressures are necessary; propagation "of bubble" detonation can be observed also at relatively low speeds.

CHAPTER V

EXCITATION OF BURNING AND DETONATION OF EXPLOSIVE SUBSTANCES (INITIAL IMPULSE AND SENSITIVITY OF EXPLOSIVES)

The presence of explosive properties for that or another substance determines only the potential possibility of an explosion. To realize this possibility, it is necessary to produce on the explosive an influence, capable of evoking an explosion. Such an influence is called the initial impulse.

Experience shows that for excitation of an explosion for some explosives a weak influence is sufficient, for others – stronger influences are required. For instance, nitrogen iodine explodes from contact of the point of a quill pen to it but trotyl does not explode even with the blow of a rifle bullet. In other words, different explosives possess various sensitivity to external influences. Sensitivity is the ability of an explosive to react to external influences by the appearance of burning or an explosion; sensitivity of an explosive is characterized by a minimum magnitude of the initial impulse, not necessary for excitation of explosive transformation of the explosive.

It is necessary to note that the sensitivity of a given explosive to the initial impulse of a definite form is not constant but depends on the conditions in which the impulse acts and on the characteristics of charge. In the case of a detonation, for instance, it depends on the thickness of the charge dimensions of the particles, aggregate state of the explosive and others.

The sensitivity of an explosive, especially to mechanical and thermal influences is one of the basic characteristics determining the possibility of its technical use. Chemistry knows many explosives which possess high indices of explosive action, but simultaneously also excessively great sensitivity, which excludes their application in technology. Such as, for instance, copper azide chlorate esters of glycerine and other alcohols.

In the process of production, transport and application an explosive is inevitably subjected to shocks and blows. Thus, a charge of an explosive in a shell in the moment of shooting experiences a strong shock due to its inertia, with a great sensitivity of the explosive this can lead to premature explosion of the charge of the explosive in the gun barrel. With a blow of the shell or aerial bomb against the earth, the armor or other barrier by sharp braking of the movement of the housing leads to rapid and strong compression of the charge in the head part which also may cause a premature explosion. These causes for equipment of artillery shells and even aerial bombs do not apply for nitroglycerine or nitrogelatin which possess great sensitivity, although their explosive action is significantly larger than, for instance, trotyl.

In production it is frequently necessary to heat explosives, sometimes in large quantities. If with this the possibility of local overheating is not included and the explosive possesses great sensitivity to heat, then, as the experience of industry shows, ignition can occur. The appearing burning can change to an explosion.

If such a transition always occurs, then it is simply impossible to prepare and to equip explosives in those scales, which contemporary technology requires. Therefore, as basic explosives, prepared and applied in large quantities in industry and military technology, such substances are used, which possess relatively low sensitivity to heat and to detonation and do not explode, as a rule, from ignition. The last circumstance reduces the danger of explosion during accidental ignition of the explosive or during a fire.

Small sensitivity of an explosive does not serve as an obstacle to excitation of explosion during their use, when detonation is evoked with the help of a percussion-detonator. Since a percussion-detonator can be introduced in a explosive only intentionally, then the ability of a secondary explosive to explode from this impulse does not create danger of an accidental explosion; the same mechanical influences with which an explosive can be subjected in usual conditions of production and application, are significantly weaker than the action of a percussion-detonator and, as a rule, do not lead to explosion.

If the sensitivity of explosives does not have to be too great because of their production and application, then it does not have to be too small. In real conditions changes of explosives are possible which are accompanied by lowering of their sensitivity, for instance, in the case of ammonites — their moistening or caking in the case of dynamite — their aging and so forth. It is necessary that an explosive possess a known "reserve of sensitivity" and will explode from a usual impulse even with these unfavorable changes.

For certain forms of use it is necessary to lower the sensitivity — to <u>flegmatize</u> the explosive or to increase the sensitivity — to <u>sensitize</u> explosive. Thus, for armor-piercing shells trotyl is flegmatized by the addition of paraffin, wax or other impurities. In shock compositions sometimes powdered glass is introduced for increasing the sensitivity to detonation.

The possibility of the appearance of explosive transformation as a result of the influence on an explosive of that or another initial impulse depends on the total energy content, transmitted to the substance, and on its concentration in a certain volume. We will explain the role of these two factors.

In order to evoke reaction of explosive transformation, activation energy must communicate with molecules of the explosive. Energy of the initial impulse passes directly to activation energy only in rare cases, for instance during irradiation of a mixture of hydrogen with chlorine with a light of a short wave length. As a rule, energy of initial impulse is absorbed by the explosive directly or indirectly in the form of heat and only a certain part of it passes to activation energy, i.e., directly leads to excitation of a chemical reaction. The greater this part the higher the temperature. Really, the chemical reaction rate is proportional to $e^{-E/RT}$, and this magnitude rapidly increases with an increase of the temperature. Therefore, during excitation of an explosion, for instance by heating, the more effective the given quantity of thermal energy is and gives the greater the active molecules the smaller the quantity of explosive it is concentrated in the higher the concentration of energy, in other words, the higher the obtainable temperature.

However, even the absolute magnitude of energy also has a value. In any explosive, even at room temperature, undoubtedly, disintegration of separate molecules occurs. However, this disintegration does not lead to explosion because the energy of the elementary reaction is dispersed to a large number of surrounding molecules. Formation of a certain sufficiently large number of active molecules in one place is necessary so that the self-spreading transformation may emerge.

Both these parameter of excitation of explosion are mutually connected: the greater the concentration of energy and correspondingly speed the reaction evoked by it, the less the minimum dimensions of the hearth of the reaction can be, which leads to the appearance of explosion, the correspondingly less may be the total energy of the initial impulse.

That said about thermal energy pertains also to energy of detonation, since excitation of an explosion by detonation occurs as a result of the local heating up created by it, leading to formation of hearths of reaction. To estimate the effectiveness of a detonation only by its total energy is still difficult because depending upon conditions of the detonation and properties of the substance the share of energy, absorbed by the explosive, and also its distribution, can be changed within very wide limits.

Let us turn to a consideration of different forms of the initial impulse.

§ 1. Initial Impulse and Mechanism of Excitation of Explosion

For excitation of an explosion it is possible to use various influences; thermal, mechanical, electrical, chemical, explosive, irradiation etc. If these initial impulses are characterized by their energy then it turns out that between magnitudes of energy in various forms usual equivalence with respect to the ability to evoke explosion is not observed. Explosives selectively are sensitive to separate forms of influence.

This circumstance is explained by the fact that the ability to absorb energy in a given form of it is different for various explosives depending on their physical properties and conditions, in which the influence is produced.

Thus, during heating of a nonvolatile and unmelted explosive all thermal energy communicated with it is expended on the increase of the temperature. If, however, heat is led to a volatile explosive then after achievement of the boiling point further rise of temperature stops as long as the entire substance is not turned into vapor. If, however, the same volatile explosive is heated under high pressure, then the boiling point will be increased, transition of the explosive to a vaporous state will be hampered and the energy communicating with it to a larger degree may be used for activation of the molecules.

The result of action of radiant energy will depend on the coefficient of absorption of the exploding in the given region of the spectrum and, furthermore, on the relationship of the magnitude of quantum of light of a given wave length an optimum of light of a given wave length and activation energy of the reaction of transformation of the explosive.

In the case of detonation the portion of mechanical energy, absorbed by the substance is perhaps very different depending on the properties of the explosive and conditions of detonation; with a blow by a liquid, for instance, it can be simply pressed in the sides without noticeable absorption of energy.

On the other hand, essentially is how the absorbed energy is distributed: equal distribution of it is unprofitable for excitation of an explosion.

Finally, with a blow the development of the reaction evoked by it occurs under a pressure that favors the appearance of burning and explosion. This does not occur during usual conditions of heating up. In the latter case in turn there are more favorable conditions for the development of chemical autoacceleration of the reaction since heating is more prolonged than action of detonation.

Thus, during communication of an explosive of a definite energy content the degree of absorption by its substance and the character of its distribution in it can to a strong measure depend on properties of the explosive and conditions in which the influence is produced.

Inasmuch as these properties, in general, are different then for various explosives identical conditions of influence are not equal, which is explained by the selective character of sensitivity of the explosive. Changing the condition of influence, it is possible correspondingly to change both the absolute as well as the relative sensitivity of the explosives, i.e., their location in the scale of sensitivity to the given form of impulse.

It is necessary to underline that selectivity of sensitivity by no means is absolute and by no means gives a basis to make a conclusion about the fundamental distinction in the mechanism of excitation of explosion with different influences.

Let us give several examples illustrating the selective sensitivity of explosives to different forms of initial impulse.

Lead azide has a higher temperature of detonation (~330°) than trotyl (~300°), but trotyl is much less sensitive to friction than lead azide.

A mixture, containing 60% potassium chlorate and 40% ferrous-cyanide potassium, explodes with a drop of a load of 5 kg from a height of 25 cm and has temperature of detonation of 310°C. A mixture from 60% potassium chlorate and 40% sodium hyposulphite has a smaller sensitivity to detonation — explodes with a drop of load from a height of 100 cm, but is more sensitive to heating — detonates at 155°.

Concerning the lack of parallelism between sensitivity to detonation and heating pertains also to the fact that temperatures of detonating of explosives, applied in technology, differ no more than twice when the energy of a blow, provoking explosion, the same explosives differ approximately by 90 times. This is explained in the first place by the essential distinction of conditions of the appearance of an explosion during slow heating (detonation) and a blow.

If one compares with sensitivity to a blow not the temperature of detonation, but inflammability and with that under high pressures, then among these characteristics a closer conformity is observed.

Non-conformity in sensitivity is also observed with respect to other forms of the initial impulse. Thus, black powder has a higher temperature (~315°C) of detonation than smokeless powder (~200°C). However, with a beam of fire black powder ignites much easier than smokeless.

Various forms of initial impulse also differ by the form of chemical transformation of the explosive they evoke. Ignition always initially evokes burning of the explosive, stable or unstable, going into detonation. For certain explosives, an example of which is lead azide, this transition occurs extremely fast, so that the stage of burning is not attained. A percussion-detonator in contrast to a thermal impulse evokes detonation; action of the blow leads to it in the end. These circumstances should be considered during selection of the initial impulse for these or other conditions of application.

Let us consider several examples.

If an open situated cartridge of trotyl is hit by a flame, then burning occurs without noticeable mechanical effect. If, however, in a reaction is excited in it by the explosion of a percussion-detonator, then detonation with strong destructive effect occurs.

If an iron cylinder is densely filled with black powder and the powder is ignited by a safety fuse, then the charge burns and cylinder remains intact. If, however, for excitation of the reaction a percussion-detonator is used, then the powder explodes and the cylinder scatters into a large number of pieces.

Slow heating of ammonium nitrate saltpeter with moderate temperatures leads to its calm decomposition into ammonia and nitric acid, which flows with heat absorption and is not capable therefore of giving an explosion. During the action of a strong detonator, ammonium nitrate detonates with disintegration into nitrogen, water and oxygen with a great energy release.

The basic forms of initial impulse are:

1) thermal impulse (heating up and igniting of the explosive);

2) mechanical impulse (blow and friction);

3) concussion during a shot and during a blow against an obstacle;

4) explosive impulse;

5) action on the explosive of ions, electrons, neutrons, nuclear fragments and ultrasonics.

1. Excitation of Explosive Transformation by Thermal Impulse

The appearance of detonation of an explosive at a constant temperature or slow heating

If one were to place an explosive in a thermostat with a constant or slowly increasing temperature, then in a certain time it is possible to observe detonation. The mechanism of the appearance of detonation in such conditions, when everything attached to the explosive is heated slowly and therefore evenly, in basic features is near the mechanism of thermal explosion, considered above (see page 73).

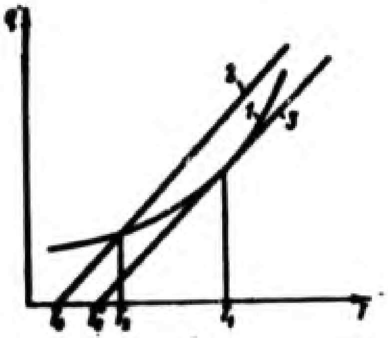

Fig. 5.1. Relationship between incoming heat and heat withdrawal during heating of an explosive. 1) incoming heat; 2 and 3) heat withdrawal.

Let us assume (Fig. 5.1) that during slow heating a temperature of the thermostat is attained equal to T_0. The temperature of the explosive will be somewhat higher at the expense of self-heating up, caused by exothermic chemical transformation of the explosive and balanced by heat withdrawal from the explosive to the thermostat. From Fig. 5.1 it is clear that the equilibrium of incoming heat q (curve 1) and heat withdrawal (straight line 2) will occur at a temperature of the explosive T_2. With a growth of T_0 the speed of chemical transformation and incoming heat rapidly increases and above a certain value of $T_0 = T'_0$ the curve of incoming heat 1 at all temperatures, which the explosive takes as a result of self-heating up, lies above the straight line of heat withdrawal 3; heat withdrawal now can no longer compensate for incoming heat, rapid progressing self-heating up of the explosive occurs, leading to a sharp acceleration of its transformation — ignition appears. The minimum temperature of the thermostat, at which ignition occurs, is called the temperature detonation of the explosive; this temperature can serve as one of the indices of sensitivity of an explosive to the action of heat.

Thus, the temperature of detonation is that minimum temperature, starting from which the curve of incoming heat at the expense of exothermic transformation of the explosive goes above the straight line of heat withdrawal.

If during identical setting of experiments the temperature of detonation of various explosives is determined, then the condition of heat withdrawal for them will be distinguished little. The basic characteristics of explosives, which determine the temperature of detonation in the considered conditions, are the speed of reaction and its thermal effect. The development of chemical acceleration of the reaction also is of essential value; if this acceleration is great, then the minimum temperature of detonation flash can strongly decrease with an increase of the duration of heating. The development of a chemical self-heating reaction conditions the appearance of delays of detonation, which in this case, in distinction from that which occurs during thermal autoacceleration, is perhaps very great.

The temperature of detonation depends on the dimensions of the charge. If one were to determine this temperature, consecutively decreasing by the batch of the explosive, then, starting with a certain minimum batch, disintegration, other things being equal will pass without detonation. This is explained by the fact that incoming gas is proportional to the volume of the explosive and heat withdrawal – to its surface. The relation of the surface to the volume is even greater the less the given form of charge of the batch of explosive.

The speed of heating also influences the temperature of detonation. If one were to heat an explosive slowly, then detonation appears at a lower temperature. This is caused by the fact that with an increase of the time of heating up to a certain given temperature the reaction of disintegration will occur to a great degree, the concentration of products of disintegration will be higher accelerating the reaction, and correspondingly a greater speed of the latter. If, however, heating is conducted too slowly, then detonation can not quite occur, since a large part of the explosive will be decomposed in the region of low temperatures; by achieving a high temperature the quantity (or concentration) of the explosive will already be so small that there will be nothing to explode.

The influence of conditions of development of chemical auto-acceleration also explains the paradoxical phenomenon of decomposition without detonation of certain explosives during rapid heating to a high temperature, exceeding the usual temperature of detonation. Thus, if nitroglycerine is introduced into a test tube, heated to 205-210°C that a sharp explosion occurs, splitting test tube into small pieces. At a temperature of 230°C or above only rapid decomposition with hardly an audible sound occurs. Similar phenomena are also observed for trotyl. If a small batch of trotyl (0.05 g) is put in a test tube, heated to 320°C then during every experiment detonation occurs. If, however, the temperature of the test tube is increased to 380°C a flash is not observed during every experiment, and at 400°C all experiments give flameless decomposition. These phenomena are explained in the following way. During rapid achievement of a high temperature, exceeding the boiling point of the explosive, it is turned into vapors, the detonation of which corresponds to their lower density and smaller autoacceleration of disintegration appears more difficult than detonation of a liquid. During slower heating, still attaining the boiling point, the explosive to a noticeable degree is decomposed; in this case the concentration of the accelerating reaction of products is significant, as a result of which detonation occurs. The volatility of the explosive plays a large role, more exact, the relationship between volatility and the chemical reaction rate in the liquid phase. If the volatility is great and chemical reaction rate small, then during strong heating of the explosive rapidly, before a chemical reaction, is developed in a liquid, it is turned into a vapor. In this case the appearance of detonation is caused wholly by the chemical transformation into the gas phase.

If, however, volatility is small, then development of the chemical reactions always starts in a condensed phase and renders a determining influence on the appearance of detonation. In accordance with that said for difficult volatile explosives, for instance tetryl, the described phenomenon, sometimes called the "upper temperature limit of detonation," is not observed.

Thus, the temperature of detonation is not constant for explosives, but depends on all factors, affecting heat withdrawal (magnitude and form of charge of the explosive, thermal conduction, thickness of shell, etc) and the speed of the reaction (pressure, more exact, the concentration in the case of explosive gases, the condition of development of self-accelerated reaction and others). Therefore, a comparison of sensitivity of explosives to heating by the temperature of their flash is possible only in that when this temperature is determined at identical conditions for all compared explosives.

The character of detonation for various explosives is different: lead azide and certain other initiating explosives give detonation;

a similar character of detonation is also observed for nitroglycerine and dynamite; detonation of the majority of other nitroesters and nitro compounds has a less sharp character.

These distinctions are conditioned by the following causes. Essentially detonation is a burning explosive. The distinction from the usual conditions of burning consists that during detonation the explosive inflames as a result of self-ignition, but not from external ignition which burns an explosive heated to a high temperature and, finally, in the fact that a pure substance is not burning, but one more or less diluted by the products of disintegration, in particular, those, which accelerate disintegration. The character of detonation depends on the degree of stable burning in these conditions. If burning is stable, then detonation is not accompanied by an explosion. With a sharp combustion instability the intensity of detonation essentially increases within the limit up to the appearance of detonation. If the explosive has a high viscosity, stabilizing the burning, then the possibility of lowering this viscosity as a result of an increase of temperature and flow of chemical processes has an influence on the character of detonation. For this reason gelatins of nitroglycerine and nitrocellulose with content of the latter of less than 60%, burn very stably at usual temperatures, at certain conditions of slow heating they give very sharp detonation.

Appearance of burning of explosives during igniting (inflammability of explosives)

If to the surface AB of a volatile explosive (Fig. 5.2) a flame is presented, then the temperature of it T will be rapidly increased and the boiling temperature T_k will be attained quickly, vapors will be formed. Further heating will lead to the ignition of vapors, from burning of vapors the explosive will start burning. However, not all conditions of ignition of vapors are sufficient so that the explosive is inflamed and continues to burn after removal of the igniting flame. The temperature of the surface layer of the explosive after removal of the external flame will be determined by two processes: communication of heat from the igniting vapors and heat withdrawal in the depth of the substance. At a given pressure — constant magnitude, heat withdrawal is determined by a gradient of the temperature near the surface of the explosive. If heating of the explosive occurs very fact, then the curve of the temperature drops in the depth of the substance steeply (Fig. 5.2a) and heat withdrawal will be more. Heat withdrawal can appear more incoming heat, then the surface AB will be cooled and burning of the explosive from ignition of vapors will not occur. If heating of the explosive occurs slower, then up to the moment of achievement on its surface of the boiling point T_k the substance will be heated to a sufficient depth (Fig. 5.2b), the curve of change of temperature will become more hollow and heat withdrawal will be exactly equal to incoming heat. Thus, if heating of an explosive occurs with the same speed, with which it goes during stationary burning, then ignition immediately leads to stable burning with a normal speed for the given conditions (pressure and initial temperature). In the case, when heating of the surface occurs even slower, the gradient of temperature in the explosive in the moment of ignition will be less than at stationary burning (Fig. 5.2c); heat withdrawal to the depth of the explosive will be less, incoming heat will remain as before and burning will go correspondingly faster. At the expense of this the curve of the change of temperature in the explosive will become steeper and will take a form, corresponding to stationary

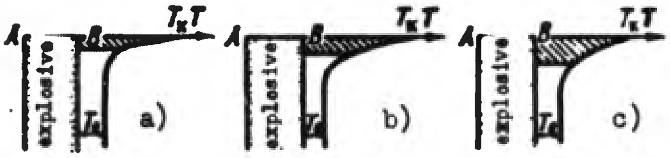

Fig. 5.2. Change of thickness of a heated layer during ignition depending upon the intensity of heating. AB — surface of the explosive. a) gradient of temperature larger than during stationary burning; b) gradient of temperature corresponding to stationary burning; c) gradient of temperature less than during stationary burning. [к = k = boiling]

burning; the burning rate will decrease with this to its stationary value.

If in the heated layer a chemical reaction does not occur, then during stationary burning the temperature at distance x from the surface of the explosive is determined [see formula (4.12)] by the expression

$$T = T_0 + (T_k - T_0)e^{-\frac{ux}{\varkappa}}, \tag{5.1}$$

where u — is the burning rate, T_k — temperature on surface of the explosive; in case of volatile explosives T_k is the boiling point; x — the temperature of transfer of the explosive.

A condition of normal ignition can be considered as formation by a external heat source of a heated layer of the explosive with the above-indicated distribution of temperature. The reserve of heat Q, which must communicate with the explosives for creation of such a heated layer can be a measure of the inflammability of the explosive. The less this reserve, the easier the explosive ignites, the greater its inflammability. The reserve of heat is calculated by the equation

$$Q = \int_0^\infty c_p\rho(T - T_0)\,dx. \tag{5.2}$$

Placing the value of T from (5.1) and considering that $x = \frac{\eta}{c_p\rho}$ after integration we obtain

$$Q = \frac{\eta}{u}(T_k - T_0), \tag{5.3}$$

where η, c_p, ρ — are respectively thermal conduction, heat capacity and density of the explosive.

It is impossible, as is sometimes done, to consider the temperature of detonation of an explosive as a characteristic of inflammability. This temperature, as we have seen, is not constant and more or less differs from T_k. Further, as can be seen from the formula

(5.3), the magnitude of Q depends not only on T_k but also on the thermal conduction of the explosive and the speed of its burning, which for various explosives can be essentially different. For the same explosive (in a powdered state) thermal conduction is changed also depending on the density, wherewith a decrease of density increases burning rate, entering in the denominator of the expression (5.3) for the reserve of heat. By these causes the inflammability of relatively fast burning black powder ($u_{1\ a.t.} \approx 1$ cm/sec)[*] is significantly larger than smokeless ($u_{1\ a.t.} \approx 0.1$ cm/sec), although the temperature of detonation of black powder (~300°C) is significantly higher than for smokeless (~200°C). In exactly the same way pyroxylin and other powdered explosives in pressed form ignite significantly more difficult than the same explosives in a friable powdery state. By the same causes the inflammability of moist pyroxylin is less than the dry; on the contrary, igniting action of moist pyroxylin is more than the dry.

The formula (5.3) shows that inflammability depends on the initial temperature of the explosives: with its increase the necessary reserve of heat decreases. Inflammability increases with the pressure: the reserve of heat is approximately reciprocal to the pressure, since the burning rate standing in the denominator of the expression (5.3), is approximately proportional to it.[**]

Inflammability is a very important characteristic of explosives, in many cases, for instance, in conditions of excitation of explosion by a blow, it is more essential than the temperature of detonation.

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[*] a.t. = technical atmospheres [Tr. Ed. note].

[**] This last dependence explains the paradoxical phenomenon of damping of burning during a sharp drop of pressure, for instance during departure of burning powder grains from a gun barrel during a shot. The reserve of heat in a heated layer, available during burning under large pressure, turns out to be insufficient for burning to continue under atmospheric pressure, although powder with this pressure is able to burn.

The existing experimental methods of determination of inflammability (see below page 477) have a qualitative character and cannot be recognized as satisfactory.

The development of a scientifically proven quantitative method of determination of inflammability constitutes one of the urgent problems of the theory of explosives.

One of the possible ways in this direction is determination of the critical diameter for burning; the magnitude of this diameter depends on the same parameters as inflammability; the critical diameter is simply determined not only at atmospheric, but also at heightened pressures by various methods. For instance, using conical charges and establishing the diameter, at which burning of the charge ceases ignited from a wider face.

2. Excitation of Explosive Transformation by Mechanical Impulse

Mechanism of appearance of explosion during a blow and friction

The process of excitation of an explosion by mechanical impulse is significantly more complicated than thermal. Two basic points of view on the mechanism of this process have been advanced. One of them allows that a blow on an explosive leads to its heating up, which excites disintegration of the explosive. The side of the other point of view considers that a explosion during a blow on an explosive appears directly as a result of its compression. Deformation of molecules or the crystal grid of the explosive evokes chemical transformation similarly as it evokes heating up.

In confirmation of the second point of view are the facts that an increase of pressure can affect the chemical reaction rate not only in gases, but also in condensed substances which in many cases of parallelism between sensitivity of the explosive to a blow and temperature of flash there is no detonation, which finally has turned out to be possible (in 70% of the experiments) to evoke an explosion of nitrogen iodine (according to Eggert), subjecting its static compression to a pressure of 5,000 a.t.. As an additional argument in favor of these views it was shown that the energy of a blow exciting explosion, in certain cases is insufficient for heating up the explosive to the temperature of detonation.

However, results of experimental research of recent times speak against the hypothesis of direct excitation of explosion by a blow. Thus, Ryabinin, and later Bouden studied the action of high pressures on thermal disintegration of a number of explosives and established that pressure, as a rule, not only does not accelerate, but in a number of cases noticeably delays disintegration.

Thus, at a pressure of 45,000 a.t. barium azide is decomposed 58 times slower than at atmospheric pressure. In exactly the same way the speed of disintegration decreases with an increase of pressure of lead azide and tetranitrate. Experiments with lead trinitroresorcin showed that its disintegration is somewhat accelerated at high pressure; the speed of decomposition of mercury fulminate at high pressure in the beginning of disintegration is higher and then becomes less than at atmospheric pressure. In general, even such a high pressure as 45,000 a.t. weakly affects the disintegration rate and moreover for the most part decreases it.

Still more convincing are the results of experiments of Bridgman, who subjected explosives (trinitrotoluene, nitroguanidine, ammonium picrate) to compression with static pressures up to 100,000 a.t., i.e., rear pressures, taking place during detonation; not for one of these explosives such pressures even in the presence of a certain deformation of shift led to explosion.*

In its initial form, the hypothesis about heating up of explosives, evoked by direct transition of all energy of a blow into heat is also not a basis for the cause of the appearance of explosion. This hypothesis does not maintain even such an elementary check, as calculation of the conformity of energy of the blow, sufficient for excitation of explosion to the quantity of thermal energy, necessary for heating up the explosive to temperature of detonation.

For certain low-sensitive explosives, indeed, energy of the blow turns out to be comparable with the necessary expenditure of heat for heating the explosive to detonation. Thus, trotyl explodes, according to Kholevo, during a drop of a load of 5 kg from a height of 50 cm, i.e., with an energy of blow of 2.5 kgm (a batch of trotyl is equal to 0.03 g, heat capacity of it is ~0.3 cal/g degrees). Energy of blow constitutes $\frac{2.5\cdot 1000}{427} = 5.85$ cal; at the expense of this energy trotyl could be heated to

$$\Delta t = \frac{5,85}{0,03\cdot 0,3} = 650^\circ.$$

The temperature of detonation of trotyl in usual conditions of its determination constitutes nearly 300°C. Thus, if one were to allow that energy of the blow is wholly used for heating the explosive, then this energy would suffice in this case for achievement of the temperature of detonation. If, however, such a calculation is done for mercury fulminate (or other explosives close to it by sensitivity), which can explode during a drop of a load of 2 kg from a height of 2 cm, then possible heating up will constitute a total of 24°, i.e., will be absolutely insufficient for achievement of the temperature of detonation (160-170°C). With this, experiment shows that only a small part of energy of the blow is absorbed by the explosive, and other parts of it are absorbed by metal of the anvil, firing pin, is expended on the rebound of the stricking load, etc.

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*At a pressure of 50,000 a.t. they were tested and as a rule did not explode, even in the presence of deformation of shift, α-trinitrotoluene, picric acid, tetryl, hexogene, tetranitrate, α- and β-nitroguanidine.

Furthermore, the duration of a blow is much less than duration of heating, necessary for excitation of detonation of trotyl or mercury fulminate at the above-indicated temperatures. With a small duration of heating, the temperature necessary for obtaining of detonation is even higher above.

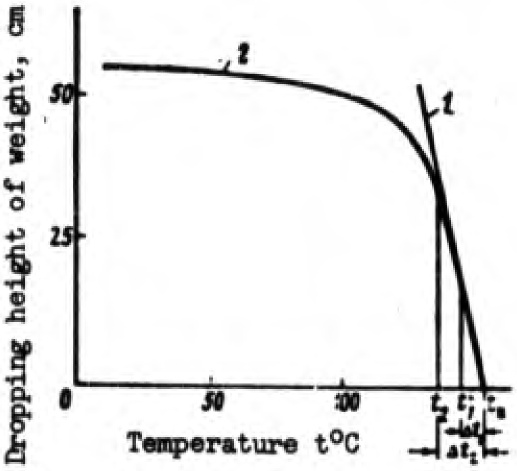


Fig. 5.3. Dependence of sensitivity of mercury fulminate to a blow on the temperature according to Taylor and Will. 1) Straight line, corresponding to the condition $H = H_0(t_B-t)$. 2) Curve, built on experimental points.

The noncorrespondence between energy contents, necessary for excitation of an explosion by a blow and for heating an explosive to the temperature of detonation can be by-passed, allowing that during a blow not the entire mass of the explosive is heated but only its thin layer, on which the blow acts directly. For checking this assumption Taylor and Will studied the influence of the initial temperature of an explosive on its sensitivity. Actually, if the role of the blow is included only in heating up of the entire batch of explosive or its film to the detonation temperature, then, obviously, a direct ratio must be observed for the difference

$$\Delta t = t_B - t$$

(where t — is temperature of the explosive, t_B — the temperature of detonation) and the necessary work of the blow. In other words, the dependence of the necessary for excitation of explosion of the work of the blow H on the temperature of the explosive t would be expressed by a straight line of the form

$$H = H_0(t_B - t)$$

(Fig. 5.3 straight line 1). The results of experiments of the given researchers give this dependence in the form of a curve (see Fig. 5.3, curve 2) which, in their opinion, excludes the possibility to explain the appearance of explosion during a blow as local heating up of the explosive.

However, this conclusion cannot be considered correct. Results of the experiments of Taylor and Will show only that the action of a blow cannot be considered simply as the direct transition of energy of the falling load to heating up the explosive.

At present the most founded hypothesis, explaining excitation of explosion during a blow and friction, is the hypothesis of local heating up which appears in an explosive with these influences. If the dimensions of the hearth of heating up and the attained in it temperature are sufficiently great, then ignition of the explosive occurs. The appearing burning can change to explosion.

Way of formation of hearths of heating up during a mechanical influence on an explosive

Mechanisms of the appearance of hearths of heating up can be different. The basic ones of them are:

1) friction between particles or layers of the explosive during displacement of them relative to one another, evoked by a normal or slipping blow;

2) friction between metallic (or other) hard surfaces, among which is a layer of explosive; heating up of metal, caused by this friction, evokes heating up in the explosive;

3) friction between hard and refractory particles, if they are present in the explosive, with displacement of them relative to one another, evoked by a normal or slipping blow. Heating up can also appear from friction of the shown particles against the metal; heating of particles detonates heating up in the explosive;

4) compression of bubbles of gases or vapors, contain in an explosive, at shock compression of the latter.

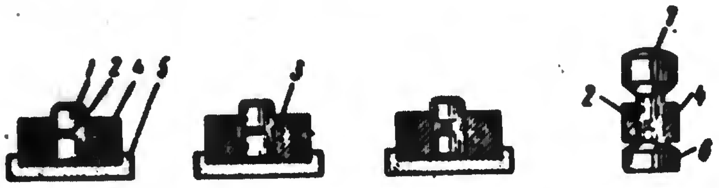
Let us consider each of the shown mechanisms of the appearance of hearths of heating up and corresponding conditions of excitation of explosion.

The appearance of hearths of heating up at the expense of friction between particles or layers of an explosive during its flow. A general picture of the appearance of explosion during a blow by such a mechanism of the formation of hearths of heating up was well-developed by N. A. Kholevo.

Excitation of explosion by a blow on a layer of explosive, laying between flat surfaces of the anvil and firing pin, includes several stages. First is the compression of the explosive. If compression is sufficiently great, there is no manifold and explosive substance with a leak, then its flow occurs. The speed of flow of various layers of the compressible charge of the explosive is different. Layers of substances, adjacent to the anvil and firing pin, do not move, the most remote layer from them moves fastest of all. Due to the distinction in the speed of flow between layers of the explosive, friction appears and, correspondingly, heating up. The biggest heating up, obviously, will appear where there is maximum gradient of the speed of flow.

Besides the gradient of the speed of flow, the magnitude of heating up is determined also by the coefficient of internal friction of the explosive, which in turn depends on the pressure and increases with its increase.

All of these factors in totality give a unique picture of the behavior of explosives with various physical properties and during different conditions of a blow. For an illustration we will consider the results of tests of sensitivity of explosives to a blow in instruments of various construction. The method of these tests will be described below in greater detail (see page 456). Sketches of the instruments are represented in Fig. 5.4.



a) b) c) d)

Fig. 5.4. Instruments for determination of the sensitivity of an explosive to a blow by a falling load. a) Instrument No. 1 (according to Kholevo); b) Instrument No. 2; c) Instrument for testing according to GOST [All-Union Government Standard] 2065-43; d) Instrument according to Kast. 1) steel rollers with a diameter of 10 mm; 2) explosive; 3) groove; 4) directing casing; 5) pan; 6) stamp anvil, diameter of working surface is 8 mm; 7) stamp firing pin with a diameter of 8 mm.

We will compare results of tests in instruments No. 1 and 2 according to Kholevo (Fig. 5.4a and b). Instrument No. 2 differs from Instrument No. 1 by the presence in directing casing of a groove on the level joint of the butt of both rollers, facilitating flowing of the explosive during a blow. In instrument No. 1 an explosive can go only in the gaps between rollers and the directing casing. Since these gaps are usually very small, then the possibility of flowing of an explosive in instrument No. 1 is much less than in instrument No. 2.

Imagine two explosives, strongly differing by fluidity, for which the appearance of explosion occurs at identical characteristics of local heating up. If one were to test the more fluid explosive in instrument No. 2, then it easily, with a small pressure, goes in the groove. The coefficient of internal friction will not increase, since during the flow a high pressure does not appear. Due to this, although the exhaust velocity and its gradient will be great, heating up will be insignificant. If the same explosive is tested in instrument No. 1, then the narrow gaps between the rollers and casing will limit the flow of the substance, during a blow in the explosive a large pressure will appear, the coefficient of internal friction will be increased and, although the exhaust velocity will be less, heating up will be more than in instrument No. 2 and correspondingly the frequency of explosions will also be more.

If, however, a difficult-flowing explosive is tested in instrument No. 2 then it will go in the groove, but since the coefficient of internal friction is great, then heating up, and consequently, also the frequency of explosions will be great. If the same substance is tested in instrument No. 1, then it will not flow, and without flow it will not heat up, and consequently also explosion.

Thus, two substances with identical kinetic and thermochemical properties, but distinguished by fluidity can in different conditions of a test conduct themselves in different ways. The least heating up and least frequency of explosions will be observed in the two extreme cases, when the speed of flow is great, but pressure is small, and when the speed of flow is very small, although the pressure is great. The biggest frequency of explosions will be obtained with several intermediate conditions, when the speed of flow is significant and the pressure is not too small. Optimum conditions of flow will be different for various explosives, even if inasmuch as the fluidity of them is essentially different.*

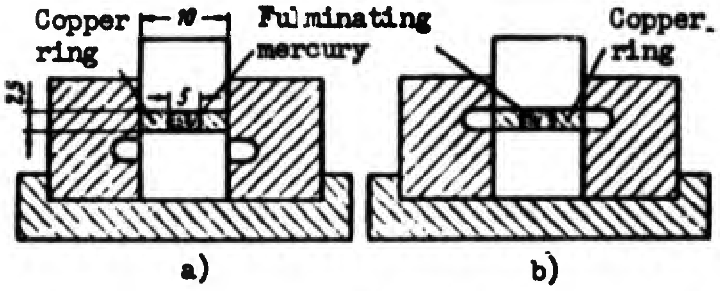


Fig. 5.5. System of the experiment of Kholevo on excitation of explosion of mercury fulminate by a blow.

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*The large influence on the effective fluidity of an explosive during a blow is the ability of the substance to be melted without strong decomposition; transition of the substance, even partial, into a liquid state sharply increases its fluidity.

In Table 5.1 (composed basically according to Kholevo) are given results of comparative tests of different explosives in instruments No. 1 and 2, showing the distinct influence of differences in fluidity on the frequency of explosions.

Thus, nitroglycerine in instrument No. 2 in certain conditions of the test does not give explosions, in instrument No. 1 the frequency of explosions is equal to 100%.

Conversely, pyroxylin in instrument No. 1 (with an energy of blow of 1.2 kgm) does not give explosions, but in instrument No. 2 80% explosions is obtained; lead styphnate in instrument No. 1 does not give explosions, but in instrument No. 2 gives 100% explosions.

The especially graphical value of the flow of a substance as a necessary condition of the appearance of explosion during blow can be seen from the experiment of Kholevo, the system of which is shown in Fig. 5.5. In a copper ring a small batch of such a sensitive explosive as mercury fulminate was pressed. During consecutive blows by load of 10 kg, dropped from heights of 10; 25; 50; 75 and 100 cm, according to the instrument used, as is shown in Fig. 5.5a, an explosion did not occur. After the last blow, rollers with casing were turned and the casing moved downwards, as a result of which the ring with mercury fulminate appeared against the groove and during the blow could be pressed in it (Fig. 5.5b). The prepared instrument thusly was subjected to a blow from a height of 15 cm; with this an explosion appeared constantly.

Above we considered the behavior of an explosive, the fluidity of which is small, but still sufficient so that it flowed in those facilitated conditions of flows, which were created in instrument No. 2.

Table 5.1. Results of Tests in Instruments No. 1 and 2 of Different Explosives in Pure Form and with Impurities having Variable Fluidity

Explosive	Energy of blow, kgm	Frequency of explosions in %	
		Instrument No. 1	Instrument No. 2
Nitroglycerine	2.0	100	0
Pyroxylin No. 2	1.2	0	80
Pyroxylin No. 2	2.5	30	100
Pyroxylin No. 2 with paraffin (95:5)	2.5	100	0
Lead styphnate	2.0	0	100
Lead azide	5	0	4
Mixture of lead azide with paraffin (97:3)	5	16	56
Trotyl	4	30	0
Trotyl	1	0	0
Mixture of trotyl with silicon oxide (70:30)	1	80	0
Mixture of trotyl with silicon oxide (50:50)	1	0	70
Trinitroxylene	4	70	0
Trinitroxylene	1	0	0
Mixture of trinitroxylene with silicon oxide (70:30)	1	20	30
Mixture of trinitroxylene with silicon oxide (50:50)	1	0	100
Hexogene	4	100	100
Hexogene	1	30	40
Mixture of hexogene with silicon oxide (70:30)	1	20	100
Mixture of hexogene with silicon oxide (50:50)	1	0	60
Tetryl	4	95	0
Black powder	4	35	70

However, it is possible to imagine an explosive with so small a fluidity that it will not flow not only in instrument No. 1 but also in instrument No. 2. Lead azide conducts itself in this manner (see Table 5.1). The fact that the absence of explosions is caused namely by the low fluidity, can be seen from the results of a test of a mixture of azide with a small quantity of paraffin (3%), when with those same conditions of test the frequency of explosions, especially in instrument No. 2, increased significantly.

This result from first glance contradicts the experience of industry. As it is known, in technology for lowering sensitivity to mechanical influences paraffin and similar substances,* are used which cover crystals of the explosive with an inert film and soften the friction between them. However, this seems contradictory. Blows with which an explosive can be subjected in practical conditions, are as a rule, not normal, but to a larger or smaller measure slipping. With a slipping blow the displacement of particles of the explosive relative to one another or relative to the firing pin appears compulsorily and is not limited by the flowing explosive. Paraffin, enveloping the particle of the explosive, decreases the coefficient of friction and therefore hampers the appearance of local heating up during displacement of particles.

Actually, experiment shows that the presence of paraffin, increasing the frequency of explosions during a blow on copra, leads to an essential decrease of this frequency in conditions of friction.

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*From such substances, besides paraffin, wax, cerezine, vaseline, camphor, fatty oils, especially castoric are used. The sensitivity of an explosive is also lowered by water, acetone and other non-explosive liquids.

Kholevo showed that an analogous change of sensitivity to a blow is observed during the addition of paraffin to many difficult flowing explosives; with this the frequency of explosions in instrument No. 1 is usually increased, and in instrument No. 2 reduced. Such an influence of paraffin and similar deterrents is observed when the fluidity of a pure explosive is less optimum in condition of instrument No. 1 and more optimum under conditions of instrument No. 2. If, however, there is a substance with relatively great fluidity, then in this case the addition of paraffin can decrease sensitivity not only to friction in instrument No. 2, but also in instrument No. 1.

The influence of the flow of an impurity has a decisive influence on the coefficient of internal friction, which it lowers. If this lowering favors the appearance of hearths of ignition, then the sensitivity of the explosive is increased and conversely.

Besides the influence of viscous impurities on the coefficient of internal friction, one should also consider the circumstance that covering the surface of crystals with an inert film, the impurity hampers not only the appearance of hearths of ignition, but also their development, and also transmission of ignition from one particle to another.

What we said pertains to impurities, which increase the fluidity of explosives. It is natural that impurities, which decrease the fluidity of explosives can also influence sensitivity.

It is known that the impurity of small quantities of solid particles of refractory mineral substances, for instance silica, alumina, magnesium oxide and so forth, increase the frequency of explosions of many explosives during test on copra. Kholevo showed, however, that if these impurities are introduced in a thin-dispersed form and in significant quantities in such a manner that the fluidity of the substance is strongly decreased, then the frequency of explosions can not only be increased, but also decreased and with this to a various degree for various explosives and conditions of test. Thus, if to trotyl, not giving (during certain conditions of test) explosions in instrument No. 1, 30% thin-dispersed silicon oxide is added, then the frequency of explosions increases up to 80%; with 50% addition the frequency of explosions drops to zero. In instrument No. 2 the frequency of explosions with 0 and 30% addition is equal to zero, with 50% it increases to 70%.

Conversely, less fluid hexogene in instrument No. 2 in the absence of impurity give 40% explosions, with 30% impurity 100% explosions, but with 50% the frequency of explosions decreased to 60%.

Above we indicated, that the pressure, appearing during a blow in an explosive, affects a coefficient of internal friction and exhaust velocity, which determines the possibility of the appearance of local heating up. However, pressure renders a large influence also on the further fate of the appearing heating up. As we have seen in § 1, the inflammability of an explosive to a significant measure depends on the pressure. The more pressure, the less reserve of heat in the heated layer, starting from which burning can spread. The action of local heating up, appearing as a result of friction, most closely corresponds to conditions of ignition of an explosive with brief external heating. Therefore, pressure in an explosive, attained during a blow, the duration of its existence and speed of the drop render a large influence. They determine, whether local heating will lead to ignition of the explosive, whether this ignition will evoke burning and whether burning will change to an explosion.

If the pressure, created by a blow, is brief and drops too fast, then the appearing burning can dampen. The reserve of heat in the heated layer, sufficient for burning at a high pressure, can appear insufficient for burning to continue at a low pressure. Experiments of Bouden show that sometimes burning, appearing during a blow, is dampened, not spreading on all to the entire explosive. It is clear, for the same reason during tests on copra frequently propagation of the appearing hearths of burning is observed only on a small part of the batch of explosives.

Thus, pressure renders a threefold action on the appearance of an explosion during a blow: it evokes the flow of the substance, changes the coefficient of internal friction and affects the rate of the appearing during the flow of hearth of chemical reaction. At present it is impossible without experiment to establish, which of the two last influences has in that or another case the greatest value.

In the entire preceding consideration of the excitation of explosion by a blow the basic attention was allotted to the role of physical properties of the explosive and conditions of the test. This by no means considers that the chemical structure of an explosive, determining the speed of the flowing in it reactions and their thermal effect, has no value. Conversely, as Kholevo shows, if the physical properties of the compared explosive were absolutely identical, then the frequency of explosions during testing on copra would be determined only by the chemical structure. Since in reality these properties are different, then the frequency of explosions is a function of both the chemical and physical properties of the explosive. It is impossible, for instance, to judge the influence of the chemical structure, not knowing quantitatively the influence of the physical properties. This is all the more just that the influence of physical properties of an explosive and conditions of tests, as appears from the above mentioned examples perhaps is very significant. Therefore, one should consider erroneous the attempt of certain researchers to consider the chemical structure as the only factor, determining sensitivity of explosives.

Simultaneously one should consider that the chemical structure and the thermochemical and kinetic properties of the substances caused by it are combined with it inalienably. Therefore, their influence will appear in all conditions of the influence, when the influence of physical properties can be changed within wide limits, for instance depending on external conditions.

With a variety of factors, affecting the sensitivity of an explosive, the appraisal of it is irrelevant to conditions of the test or influence is very difficult. This difficulty is increased still by the following circumstance. Usually during experimental determination of the sensitivity it is characterized by the energy of the blow, at which a definite frequency of explosions is obtained. Kholevo justly indicated, this criterion cannot be considered because of a number of causes.

First of all during a blow on an explosive,in usual conditions of the test, only a part of the energy of the blow is absorbed by the explosive itself, whereupon the portion of absorbed energy of the blow very strongly depends on the physical properties of the substance. Thus, according to the experiments of Kholevo, during a test in instrument No. 1, trotyl absorbed almost 80% of the energy of the blow, hexogene in the same conditions – not more than 12%; especially little energy is absorbed by infusible powders, for instance carbon, sand and so forth.

Absorption of energy also depends on conditions of the blow. If, for instance, a firing pin produces a blow on a drop of water, lying on a flat anvil, then it is obvious that the water will simply be pressed with great speed, where the expenditure of energy on pressing will be small, also the pressure will be small, appearing in the water during the blow. If the blow is produced on lead, then the pressure in it will be greater, the speed of the flow less, but the expenditure of energy of blow on pressing — greater. Finally, during a blow on steel the stress will be the biggest, and the speed of deformation the least. In turn, if a drop of water is in a cylinder under a well fitted piston, then the pressures, appearing in the water during a blow, will be much larger than in the above considered conditions.

Besides the quantity of absorbed energy, the speed of its absorption and distribution in the explosive have essential value. The faster energy is absorbed and the less evenly it is distributed, i.e., the more its local concentration, the easier explosion appears.

The total energy of a blow cannot simply be characterized as excitation of an explosion, as can be seen at least from that which sometimes with an increase of energy of the blow (increase of height of drop with a given load) the frequency of explosions does not increase or even drops, which, obviously, is combined with less favorable conditions of absorption of energy and development of the explosion.

The magnitude of the absorbed energy, according to Kholevo, strongly oscillates from experiment to experiment which, apparently, also determines the relatively very large oscillations of the results observed during experimental determination of sensitivity to a blow.

The appearance of local heating up during friction of hard surfaces, among which is an explosive. Bouden experimentally showed that during friction of metal rod against a glass disk a local brief, but strong heating up occurs, which it is possible to photograph. The increase of temperature can also be observed and measured by the appearance of thermoelectromotion force, if friction is carried out between two different metals. Curve of the change of thermoelectromotion force (Fig. 5.6) is a number of consecutive peaks, the amplitude of which shows that during friction of refractory metals view high temperatures can be attained. The experiment showed that heating up of such a type are also observed when the rubbing surfaces are moistened with a liquid. In light of these observations it is natural to assume that if between rubbing surfaces there is an explosive, then the explosion of it, appearing during friction, is caused by the shown heating up.

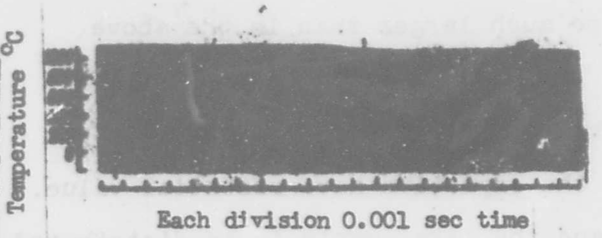

Fig. 5.6. Recording by cathode oscillograph of the thermoelectromotion force, appearing between a slider of constantan and a polished steel surface. Normal pressure of 500 g; speed of slip 300 cm/sec; rises of temperatures are significant and very brief.

The appearance of hearths of heating up during friction of alien hard particles, contained in an explosive. Heating up for this reason can appear during slipping, and also during a normal blow, when it evokes flow of an explosive, containing hard impurities. It is known that even small quantities of certain hard impurities can increase the sensitivity to a blow.

Table 5.2. Influence of a Content of Sand on the Sensitivity of Trotyl to a Blow Load of 10 kg, Height of Drop 25 cm

Content of sand in %	Frequency of explosions in %
0.01-0.05	6
0.1-0.15	20
0.2-0.25	29

As an illustration of this influence it is possible to give the data of K. K. Snitko about the dependence of the frequency of explosions of trotyl during a blow on the content of sand in it (Table 5.2). Namely, therefore to explosives applied for equiping ammunition, rigid requirements are presented with respect to the lack in them of sand or other hard impurities. Thus, according to the standard in trotyl a content of mineral impurities not more than 0.10% is allowed; in more a sensitive explosive — tetryl — a content of mineral impurities of not more than 0.05% is allowed, while silica (sand) should not be more than 0.015%.

In the question about what characteristics of hard particles determine their sensitizing action, up to recent time there has been no clarity. It is usually considered that hardness of particles plays a decisive role. However, experiments of Bouden showed that the basic property of hard particles, determining their sensitizing action, is not hardness, but the temperature of fusing. Particles of substances, having a temperature of fusing below 400°C (for instance, crystals of nitrate and bichromate of potassium, acetate of sodium), do not increase the sensitivity of secondary explosives to a blow and friction. Thermal conduction of refractory particles is also an essential factor: the higher the thermal conduction, the less sensitizing action. Namely high thermal conduction explains the relatively weak sensitizing action of table salt, the temperature of fusing of which (804°C) lies significantly above the shown limit (400°C).

The appearance of hearths of heating up during fast compression of bubbles of gas vapors contained in explosives. Compression and adiabatic heating up of bubbles of air or another gas during a blow may be the basic cause of the appearance of hearths of heating up, especially in liquid explosives. The role of gas bubbles during a blow is explained by the fact that due to a large coefficient of compression of gases during compression of them a much higher temperature is attained than in the condensed phase. Therefore, gas pockets are hearths of appearance of burning of explosives, changing in conditions of high pressure during blow into an explosion.

The most convincing illustration of the role of air inclusions are the results of experiments of Bouden, when a drop of nitroglycerine, located on an anvil, gave the form of a ring which sharply increased sensitivity to a blow. A still sharper lowering of energy of a blow, necessary for obtaining an explosion, was observed in the case, when a flat surface of a firing pin a small deepening was made. Explosion of nitroglycerine in these conditions occurred during energy of a blow of 0.0002 kgm, whereas in the absence of a bubble of air for that is required an energy of 1-10kgm, i.e., at least 5,000 times more. The influence of air inclusions can appear also with a flat firing pin. If before the blow the face of such a firing pin is at a certain distance from the surface of the liquid explosive, then with an identical energy of blow the frequency of explosions are much larger than in the case, when the firing pin touches the explosive. This is clarified by the fact that in the first case on the surface of the firing pin with the blow bubbles of air are enclosed, heating up of which ignites the explosive.

A similar influence also appears in the case of lead azide and certain other easily inflammable explosives. This is possible to explain by the following. A high temperature is attained during compression of a gas already at small pressures. In adiabatic conditions with an increase of pressure of a total to 20 a.t. the temperature is increased almost to 500°C.

If the inflammability of an explosive is great, i.e., if the reserve of heat in the heated layer during burning is small and the explosive is able to burn at a low pressure, then the appearance of burning and explosion is possible from the heated up gas bubbles. If, however inflammability is small, then the bubble mechanism of appearance of explosion during a blow is not realized and explosion appears only at much large pressures, when the flow of a solid explosive sets in.

Additional confirmation of the role of gas pockets during the appearance of an explosion is given by experiments, at which a drop of nitroglycerine in the form of a ring was subjected to a blow at various initial pressures of the gas surrounding this explosive. In those conditions, when in nitrogen at a pressure of one a.t. 100% explosions were obtained, at a pressure of 25 a.t., the frequency of explosions fell to zero.

However, experiments in a vacuum even at insignificantly small residual pressures (10^{-5} mm mercury column) did not show a lowering of sensitivity, although in these conditions compression of bubbles of air also could not play a role, Bouden and his colleagues consider that in this case vapors of the explosive were subjected to compression and this led to their heating up and ignition, transmitted by the mass of liquid substance.

As confirmation of this assumption they consider results of experiments, at which in nitroglycerine an inclusion of explosive (methylnitrate) or nonexplosive vapors (CCl_4 and others) were artificially introduced, which also led to an increase of sensitivity to a blow. The fact that a explosion during blow on a liquid, containing bubbles, appears where it is, was shown by Bouden with the help of photographing the development of an explosion (through a transparent anvil or firing pin) on moving film.*

If the liquid is completely liberated from inclusions of gases or vapors, then heating up during a blow can appear as a result of its rapid flow between surfaces with the blows. However, in this case, many times higher energies of a blow are required than for explosion of a liquid, containing gas bubbles.

Thus, the transition of an explosive to a liquid state can lead in known conditions of a blow to a very large increase of sensitivity from the possibility of excitation of explosion by compression of gas bubbles.

3. Appearance of Explosion of Charge in the Body of a Shell on Concussion During a Shot or from a Blow Against an Obstacle

A bursting charge of an artillery shell should possess definite stability to concussions during a shot and with a blow against a barrier. For a characteristic of this stability usually originate from those stresses, which appear in a bursting charge during a shot under the action of inertial forces. If the stresses are sufficiently great in order to evoke rapid displacement and friction of the charge

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*It is interesting to note that for all studied explosives, besides lead azide, the first stage is more or less rapid burning, after the combustion of a certain point of the charge burning passes to detonation.

about the body or parts of the charge relative to one another, then besides local heating up, ignition and explosion can occur.

In simplest form calculation of inertial stresses produced on the basis of the second law of Newton

$$P_{max} = ma_{max}. \qquad (5.4)$$

where P_{max} – is the maximum value of force, from which powdered gases press on the bottom of the shell;

m – is the mass of the shell, equal to G_s/g – the weight of it, divided by acceleration due to gravity;

a_{max} – maximum acceleration, which the shell obtains.

Since

$$P_{max} = p_{max}\frac{\pi d_c^2}{4}. \qquad [c = s = \text{shell}]$$

where p_{max} – is the maximum pressure of the powder gases;

d_s – is the diameter of the shell,

then

$$a_{max} = \frac{p_{max}\pi d_c^2 g}{4G_c}. \qquad (5.5)$$

Designating $\frac{P_{max}\pi d_s^2}{4G_s}$ as n, we obtain

$$a_{max} = ng. \qquad (5\ 6)$$

where n – the so-called coefficient of overload, shows how many times the maximum acceleration of shell exceeds acceleration due to gravity.

The force of inertia F appearing in the charge during acceleration of movement of the shell, obviously attains maximum in the bottom part of the charge and is equal to

$$F = a_{max}G_c/g \qquad [s = c = \text{charge}] \qquad (5.7)$$

or

$$F = ngG_c/g = nG_c. \qquad (5.8)$$

where G_c – is the weight of the charge.

Stress f, appearing in the explosive is equal to the force which refers to the unit of area of the section of the charge, constitutes

$$f=\frac{nQ_cA}{\pi d_c^2}. \qquad (5.9)$$

where d_c — is the diameter of the charge.

The formula for calculation of the stresses, appearing in the charge during a blow of a shell on a barrier (for instance, on armor), can be conducted in an analogous way, if the speed of the shell at the moment of blow and the law of its bursting in the barrier are known.

The formula (5.9) gives the correct magnitude of stress only in the case when the charge has the form of a cylinder and fastening of it with walls of the chamber of the shell, as well as plastic flow during compression, are absent.

With fastening of the charge with walls of the body of the shell stress in charge decreases, with durable fastening — several times. In exactly the same way stress decreases in the bottom part of the charge as compared to that calculated by the formula (5.9), if the chamber has the form of a frustum of a cone. If the charge under the influence of the appearing in it stresses is expanded in a radial direction and is pressed in the walls of the body, then this increases the friction between the charge and walls and also decreases stress in the bottom part of the charge.

Of defects of a charge, which promote its deformation during a shot and can lead to premature bursts, one should note the nonuniform density of the bursting charge, the presence in it of hollows and cracks, and also sections of macrocrystalline structure. Premature breaks is also promoted by the presence of a gap between the bottom of the body of the missile and the bursting charge. This gap usually will be formed for shells, filled through the head, due to a decrease of dimensions of the charge during its cooling. The gap makes possible displacement of the charge during the shot, an explosion can also appear as a result of rapid compression of the air in the gap or a mixture of air with vapors of explosive solvents, on which varnish for covering the internal surface of the body of the shell was prepared.

Practice and research has determined that a number of explosives possess different stability to concussions during a shot or during a blow against a durable obstacle (armor, concrete and others). This is determined, on the one hand, by a difference in mechanical properties and the physico-mechanical structure of charges of various explosives, in consequence of which during action of identical inertial forces deformation is obtained different. The magnitude of deformation depends also on the durability of the body of the shell. On the other hand, an important factor is the difference in sensitivity of various explosives, in the ability of them to explode under the influence of local heating up, appearing during displacements. It is practically accepted to characterize the sensitivity of different explosives to concussions during a shot (or during a blow against a barrier) by the biggest stress in the dangerous section of the bursting charge, at which an explosion still does not appear. These biggest stresses are called <u>critical</u>.

It is necessary to underline once again that by itself stress (pressure), even very high (see § 1, Paragraph 2), cannot evoke an explosion. An explosion appears only in the case when under the action of stresses in the charge deformation occurs (shifts, blows), at which hearths of heating up can be formed. At a high pressure the ignition, appearing in the hearth of heating up, easily passes into explosion. The possibility of the appearance of an explosion is determined therefore not only from the explosive, the charge consists and what stresses appear in it, but also on the quality of equipment, form of charge, durability of fastening of it with the body and so forth. Critical stresses are characteristic of not only one explosive of which the charge consists, but also the construction of the charge, technology of equipment and other factors. The practical value of these stresses consists of that they indicate the dangerous boundary for definite constructions of the bursting charge and methods of equipment, for which corresponding tests were conducted.

During designing of shells permissible stresses, naturally, are taken lower than critical, in order to ensure full safety from the appearance of premature explosions. The available in literature data on permissible stresses for several explosives is given in Table 5.3. During use of Table 5.3 one should remember that this data is essence characterizes the property of a system, including the body of the shell, the device of the charge and sensitivity of the explosive, from which this charge consists. If the characteristic of body and charge is modified, then the value of the critical stress of a given explosive also can be changed.

Table 5.3. Permissible Stresses for Several Explosives

Explosive	Permissible stress in kg/cm^2
Trotyl	1100
Picric acid	500
Alloy of picric acid and dinitronapthalene 80/20	600
Black powder	150
Ammatol 80/20	1000

4. Action of Explosive Impulse on Explosives

The explosion of a charge of an explosive may be excited by the explosion of another charge. In a particular case, when charges are at a certain distance from each other, this phenomenon carries the name of transmission of detonation in a distance. The charge, which explodes first, is called the active, or initiating charge; the charge, which explodes under the influence of the explosion of the active charge, is called the passive, or initiated, charge.

Usually the magnitude of the minimum active charge, necessary for excitation of an explosion in certain conditions is taken for the measure of initiating action or in other words the ability of a given explosive to evoke explosion of another explosive.

In the case of initiating explosives the explosion of an active charge usually is excited by igniting.

The dependence of initiating action of initiating explosives or their chemical or physical properties is not directly determined. Below are described certain facts about the initiating action of various explosives.

An explosion of identical charges of pyroxylin was excited by different initiating explosives, in turn, the explosion of these explosives was evoked by igniting. In these conditions minimum active charges, also called limiting charges, turned out to be equal: for mercury fulminate 0.3 g, for chlorous nitrogen 3.25 g, iodine nitrogen is more 6.5 g.

For excitation of an explosion of picric acid 0.024 g of lead azide or 0.25 g of mercury fulminate are sufficient at the same time the explosion of - charge in 0.5 g nitrogen sulfide or nitric acid diazobenzene does not evoke explosion of picric acid.

The energy content, separated at an explosion of 0.25 g of mercury fulminate, is knowingly more than during the explosion of 0.024 g of lead azide; also the speed of detonation of mercury fulminate is greater, and also the volume of the forming gases during the explosion. In exactly the same way there is much more energy and quantity of gases forming during an explosion of 6.5 g of iodine nitrogen as compared to 0.3 g of mercury fulminate.

For an explanation of these observations it follows according to Wöhler to allow that during ignition initiating explosives give detonation not at once, but only after a certain period of burning. With this the length of the section of burning for different initiating substances is different. The ability to evoke an explosion is caused basically by a blow, which the products of the explosion of the active charge produce by a passive charge, i.e., the magnitude of pressure, and also the speed of its build-up. Since the force and sharpness of the blow are determined first of all by the speed of propagation of the process, then an explosive having the shortest section of predetonational burning will, other things being equal, evoke an explosion better than the other. In other words, a limiting charge of this explosive will be less than the remaining substances.

The given considerations can be explained by the following graph (Fig. 5.7), where along the axis of the abscissas is plotted the distance from the place of ignition of the charge of the initiating explosive, ignited from the face, along the axis of ordinates — the speed of propagation of the process u, obtainable in a given section of the charge. In the graph schematically are shown relationships, taking place for lead azide and mercury fulminate. In Fig. 5.7 it is clear that the speed of detonation of mercury fulminate is more than lead azide, and it has a longer section of burning. Therefore, with small charges the initiating action of mercury fulminate will be less than lead azide.

The graph of Fig. 5.7 does fully exactly depicts the phenomenon, since, apparently, the transition of burning to detonation in reality occurs not by means of a gradual increase of speed of propagation, but intermittently, (see page 269). Namely, therefore, it is possible to observe a sharp transition from initiation to rejections during lowering of the magnitude of the charge below the limit.

Even contemporary methods still do not allow with sufficient accuracy to measure the speed of detonation on very short sections, in order to give accurate experimental confirmation of the considered hypothesis. However, indirect confirmations of it are, for a number of initiating explosives (mercury fulminate, trinitroresorcin lead, cyanurtriazide) or section of burning during excitation of the explosion by a blow, an incandescent wire or spark managed to observe experimentally (photographing on moving film). In the same conditions and even during large resolving power of equipment (image converter) the section of burning in azides of lead or silver were not noted. As indirect proof of the hypothesis of Wöhler it is possible to conduct also results of very simple experiments. If several milligrams of lead azide are ignited on a hard lining, for instance on glass, then an explosion occurs with a sharp sound and strong mechanical effect; in the glass usually a hole without radial cracks is obtained. During an analogous experiment with mercury fulminate even with a batch of several tens of milligrams an almost soundless detonation without mechanical effect occurs. If, however, to the mercury fulminate a very little small crystal of lead azide is added, which by itself produces almost no mechanical action, then during igniting the mercury fulminate explodes, piercing the glass. In the last case, under the influence of the explosion of lead azide the section of burning of mercury fulminate strongly is

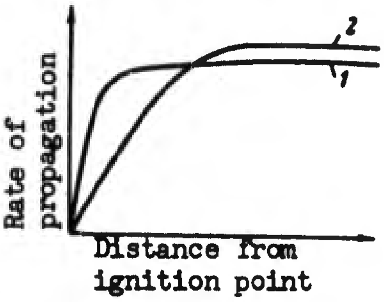

Fig. 5.7. Development of detonation during igniting of initiating explosives according to Wöhler. 1) lead azide; 2) mercury fulminate.

reduced and its burning succeeds to change to an explosion. The addition of lead azide sharply also increases the initiating action of mercury fulminate in small charges.

In the technology of explosives the impulse is accomplished mainly with the help of a percussion-detonator, which is the basic means of excitation of explosion of secondary explosives, is mining as well as in military affairs.

In its initial form the percussion-detonator constituted a small metallic case containing a small charge: 1-2 g of an initiating explosive. During igniting or incandescence of the initiating explosive detonation appears rapidly. Detonation of a percussion-detonator, placed in a charge of secondary explosive, reliably excites explosion of the latter. Invention of the percussion-detonator in 1864 constituted an epoch in the development of the application of explosives. Many substances and mixture, not exploding during action of other impulses, turned out to be able to detonate from a percussion-detonator.

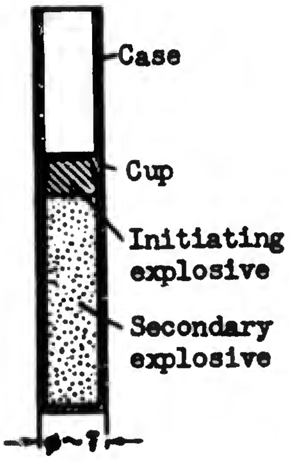

Fig. 5.8. Arrangement of a percussion-detonator.

With what is determined the high effectiveness of the percussion-detonator as a means of excitation of detonation? During an explosion the percussion extraordinarily fast forms gases, having a very high temperature and pressure; these gases produce a sharp blow on the explosive, in which is introduced the percussion-detonator. Such a blow is also a basic factor, determining excitation of explosion; temperature of gases has value only as far as it is combined with the obtainable pressure. Therefore, during selection of an explosive for equipment percussion-detonators usually are oriented to a high-explosive with great speed of detonation and density creating during the explosion a sharp and great rise of pressure.

These considerations have determined contemporary the device percussion-detonators, in which a large part of the charge of initiating substance is replaced by a secondary explosive of large brisance — tetryl, tetranitrate, hexogene and so forth. The fact that mercury fulminate during detonation in a maximum pressed state ($\rho \approx 4.4$ g/cm^3) possesses a great brisance; however in this form of it, it is impossible to apply percussion-detonators, since it turns out to be pressed "fast" and a large part of the charge burns, not detonating. Therefore, mercury fulminate is pressed in a percussion-detonators under moderate pressure (300-350 a.t.) giving a small density (2.8-3.0 g/cm^3). In such a form mercury fulminate gives rapid transition of burning to detonation but has small brisance and relatively weak initiating action. Furthermore, mercury fulminate is relatively expensive and in dry form is dangerous in circulation.

Because of these causes in contemporary percussion-detonators the charge of mercury fulminate is decreased and constitutes usually not more than 0.5 g, and instead of it in the lower part of the case is pressed to a great density a secondary explosive usually in a quantity of 1 g (Fig. 5.8). Such a combined charge with a total weight of 1.5 g renders no smaller, and even somewhat larger initiating action than 2 g of mercury fulminate with its moderate density. In order to accelerate the transition of burning of mercury fulminate to detonation, over it is pressed a metallic cup with a small central hole, through which ignition occurs. Presence of this cup hampers draining of gases, promoting an increase of pressure and, accordingly, acceleration of burning. Furthermore, the cup protects the surface of the initiating explosive from friction during introduction in the case of firewire rd and therefore decreases the danger of handling the percussion-detonators.

Instead of mercury fulminate also lead azide is used. In this case over a layer of azide a small quantity of lead trinitroresorcin is pressed — the explosive, possessing weak initiating action, but good inflammability. Such construction of the charge ensures unfailing ignition from firewire cord or electroignition. Without lead trinitroresorcin it is difficult to provide the necessary action of the percussion, as lead azide differs by comparatively low inflammability.

Percussion-detonators, containing lead azide, have a case of aluminum, since it is supposed that in the presence of mine air, containing much carbon dioxide and water vapors, is hydrolisis of azide and formation of insoluble lead carbonate is possible. With this noticeable quantities of nitrous-hydrogen acid are liberated, which in contact with copper can form very sensitive and therefore dangeous copper azide.

In the last decades in our mining affairs for the purpose of saving copper obtained significant application from mercury-fulminate-tetryl percussion-detonators in a cheap paper (cardboard) case.

5. Action of Explosives of Ions, Electrons, Nuclear Fragments, α-Particles, X-Rays and Ultrasonics

The action of electrons on different explosives was studied for the first time by Roginskiy, and then by other researchers. It has been determined that electrons evoke slow decomposition of explosives. Explosion appears only in the case when during prolonged action of a powerful electron beam strong heating up of the explosive occurs.

Thus, Bouden and Sing observed explosions of lead azides, silver and cadmium, nitrogen iodine and silver ethyne during intense bombardment of them by electrons. Replacing an explosive with potassium nitrate (point cf fusing 334°C) in the same conditions of effect of electrons, they observed fusing of nitrate which indicates the high obtainable temperature.

The action of ions, especially heavy (Ar, Hg), can, according to experiments of Kal'man and Shrenkler, evoke explosion. With this the total energy necessary for explosion decreases with the increase of stress of the field, determining the energy of separate ions.

However, according to Belyayev explosions in these experiments appeared not directly from the action of ions, but as a result of formation of a significant potential difference between the lining, on which the explosive is placed, and the negatively charged parts of the instrument with subsequent skipping of an electrical spark. During subsequent experiments of Belyayev and Khariton conducted under conditions, excluding ignition by spark, explosions during action of the flow of ions on different explosives was not observed.

Slow neutrons (number of neutrons on 1 cm^2 in 1 sec constituted for various explosives from 10^6 to 10^8) do not lead to an explosion of azides of cadmium, lithium, silver and lead, silver ethyne and iodine nitrogen even during extended (to 1 hour) irradiation.

Bombardment by nuclear fragments of U^{235} of azides of lead and cadmium also did not lead to explosion both at usual, as well as at heightened (to 290°C) temperatures. Iodine nitrogen in this case gives an explosion. The mixture of iodine nitrogen with uranium oxide spontaneously detonates without irradiation by neutrons after a twenty-minute drying, when iodine nitrogen itself in the same conditions does not give an explosion during many hours. During the action of neutrons (6000 per sec) the time up to the appearance of an explosion is reduced twice. Other studied explosives — nitrodiazobenzene perchlorate, hexamethylenetriperoxidediamine, trinitrotriazidobenzene and mercury fulminate did not detonate in these conditions of the experiment.

The action of α-particles, more exactly talking, the total radiation given by radium, was studied by Garner and Mürauer. In the case of barium azide irradiation at room temperature does not evoke decomposition and is not reflected on the character and speed of growth of these embryos. On the decomposition of mercury fulminate radiation of radium does not render an influence. Not during one of the investigated explosives, even iodine nitrogen, was an explosion obtained.

Preliminary irradiation by thermal neutrons, according to Bouden and Sing, twice reduces the induction period during thermal disintegration of lithium azide and considerably increases the disintegration rate. In the case of azides of lead and cadmium also is observed somewhat, but weaker than for azide of lithium, acceleration of disintegration. On decomposition of silver azide (in melted state) preliminary irradiation by neutrons does not have an influence.

During action of x-rays on azides of barium, lead and silver is observed slow decomposition even at room temperature, but explosion does not occur.

Convincing and graphic proof that separate elementary particles even with their very great energy are not in a state to evoke explosion of an explosive, is the fact of the existence of radioactive explosives, for instance radium azide, obtained in 1910. This explosive by properties, in particular, by stability, is similar with its analog – barium azide; the unceasing action of all forms of radiation, appearing during disintegration of atoms of radium, does not render essential influence on disintegration of atoms of radium, does not render an essential influence on the properties of radium azide as an explosive.

All this experimental data agrees with the contemporary ideas about the fact that for the appearance of an explosion it is necessary to form a hearth of disintegration, consisting of a very large number of molecules; therefore there are no bases to expect the appearance of an explosion from a blow of separate elementary particles even with their very great energy. As experiments show, the action of nuclear fragments of disintegration of uranium, the carrier of very high energy, many millions of times exceeds usual activation energies, does not evoke explosion during passage through lead azide, although with this on the way of the particle, undoubtedly, is activated and disintegrates a large number of separate molecules of the explosive. Even if one were to assume that the energy of a particle is not directly used on activation of molecules, but is turned into heat, heating an explosive up to 400°C, then the volume of such a hearth of heating up an explosive will constitute nearly $3 \cdot 10^{-14}$ cm^3, i.e., will include billions of molecules.

Thus, excitation of an explosion is combined with the appearance of a large (as compared to dimensions of the molecule) hearth of disintegration. According to data of Khariton and Belyayev about the transmission of detonation between crystals of lead azide, the diameter of a volatile particle, able to evoke detonation of a passive crystal, is of the order of 1 μ. On the basis of experiments on excitation of explosion by a blow Bouden estimates the dimensions of the hearth of heating up, necessary for exciting an explosion, is 10^{-5}-10^{-3} cm. It is natural that these dimensions depend on the nature of the explosive and its temperature. Bouden and Sing determined the dimensions of small crystals of certain initiating explosives (azides of lead, cadmium and silver), sufficient for obtaining an explosion during heating. At a temperature of 300-400°C these dimensions constitute 20-60 μ, which agree well with other appraisals, obtained in reference to conditions of a blow.

Ultrasonics with a frequency of oscillations of 10^6 per sec, according to experiments of Marinesko, evokes explosion of iodine nitrogen, silver fulminate and other highly sensitive compounds; if an explosive is alloyed or is impregnated by paraffin, then an explosion is not obtained. The action of ultrasonics is explained by the fact that it creates in its way a heightened pressure (in conditions of given experiments up to 8 a.t.), which heats the air, laying between particles of the explosive, to temperatures, exceeding the temperature of detonation. However, Khariton observed during action of ultrasonics the explosion of chlorous nitrogen, i.e., a liquid explosive, where this mechanism is directly excluded.

In conclusion one should mention the interesting phenomenon, opened by Khariton and Belyayev in the Soviet Union and Garner in England. If at a usual room temperature a container is pumped, in which there is iodine nitrogen, then with achievement of a pressure of 0.1 mm of the mercury column explosion occurs. Thus, in this case a vacuum serves as the initial impulse. The action of evacuation the English researchers is explained by the fact that with this from the surface of particles of iodine nitrogen adsorbed gases depart (in the first place ammonia), braking its disintegration.

In light of this data it is probable that explosion of iodine nitrogen with contact to it of a quill pen also is evoked by formation of the bare surface.

The appearance of an explosion during evacuation of air was observed by Apin and also liquid chlorous nitrogen; it was combined in this case with the development of a chain reaction in vapors with a decrease of pressure on the liquid. By analogy Apin explains also the appearance of an explosion during evacuation of a vessel with nitrogen iodine.

It is necessary also to note Miles' discovery of the spontaneous appearance of explosion of β-forms of azides of lead and mercury, occurring during formation of their crystals from aqueous solutions of sodium azide and nitric acid of lead or mercury, and the spontaneous explosions of the azide of bivalent mercury during cooling of its heated up crystals. The value and interest of these facts consists that they show the possibility of appearance of an explosion, not combined directly with an increase of temperature of the explosive.*

§ 2. Sensitivity of Explosive Substances

1. The Relationship Between the Chemical Structure and Sensitivity of Explosive Substances

It is obvious that the chemical structure of explosive substances [ES] (composition of molecules, nature and energy of interatomic bonds, their mutual location and influence, determining physical and chemical properties of substance) characterizes the speed of their chemical transformation during heating and the thermal effect of the corresponding reactions, and consequently also the sensitivity.

Considering the sensitivity ES to heating, we have established that one of the main characteristics is the speed of the thermal disintegration of ES. However, the relationship even between this very simple characteristic and chemical structure turns out to be very complicated.

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*One of such possibilities is the occurence of electrical charges during breakage of ES crystals. During the formation of a significant potential difference electrification can lead to sparking and ignition of ES.

It is true, the differences between various classes of ES on the whole are quite definite. Thus, nitro esters of alcohols and carbohydrates disintegrate very quickly during heating and are more sensitive to heat and shock than the nitro compound of benzene series hydrocarbons; aromatic nitro amines occupy an intermediate position. However, within the framework of one and the same class of substances, with identical types of bonds, one finds very large differences with respect to reactivity. Thus, for instance, the introduction of a fourth nitro group into benzene ring, not changing the type of bonds, lowers the stability to heating so much (especially in the presence of moisture) that tetranitro compounds up to the present time did not acquire any practical use, in spite of the fact that in terms of the force of explosion they exceed trinitro compound.

On the other hand, certain structures lead to a significant decrease of reactivity. Thus, for instance, pentaerythritoltetranitrate (PETN) is significantly more stable during heating, and also during shock than the majority of nitro esters, close to it in the energy of explosion. However, the latest studies show that these characteristics of pentaerythritoltetranitrate result from the fact that it is a solid at ordinary temperatures. In the liquid state the speed of thermal disintegration of ten is near to nitroglycol and nitroglycerine. Thus, in this case the effect of the chemical structure appears not directly but indirectly — through its influence on the melting point of the substance. Trinitrotriazobenzene has significantly larger stability during heating than dinitrotriazobenzene, at the same time it exceeds significantly dinitrotriazobenzene in energy content. An especially low rate of thermal disintegration is displayed by cyclotrimethylenetrinitramine (hexogene) and cyclotetramethylentetranitramine (octogene), which are close to trotyl in chemical stability, but they greatly exceed it in the energ of explosion. The stability of aromatic nitramine – tetryl is much lower. Strongly endothermic prussic acid and some of its salts posse very low sensitivity to detonation.

All these facts are explained by the mutual influence of atoms and groups, which can change the stability of molecules significantly. Unfortunately, this influence is still inaccessible for complete calculations and the important technological problem – the search of more effective, but moderately sensitive ES – is resolved only experimentally.

It is necessary to add that the negative value of great thermal sensitivity can be increased sharply by the self-accelerated nature of disintegration. In this case spontaneous ignition and explosion can set even at relatively low temperatures, down to normal storage temperatures if the thickness of the ES layer and duration of its storage at such temperatures are great.

The quantitative characteristic of self-acceleration of the disintegration of ES also cannot be reliably predicted at present. Moreover under different conditions, the self-acceleration for one and the same ES can appear in various degrees. Consequently, in most cases it is impossible to predict the extent of slow disintegration of a new explosive compound in any other way except through analogy, although its magnitude, determined in the first place by the activati energy is combined in the simplest with the chemical structure of ES.

Even less ready for scientific analysis is the question on the relationship between the chemical structure and sensitivity of ES to other technically important forms of initiating impulse – shock, friction, primer cap etc. The excitation of explosion in these case can depend to a great extent on the physical properties of ES and the conditions of interaction. The absence of parallelism between the sensitivity to different forms of initial impulse underlines the complexity of phenomenon, which it is impossible to consider as dependent only on the chemical structure of ES as such, independently of the complex of its physical properties and test conditions.

It is easy to show by a number of examples that the chemical structure by itself is only one of the factors which determine the sensitivity of ES. Thus, certain substances (for instance, Berthollet's salt and red phosphorus), are not explosive by themselves, but they produce mechanical mixtures, possessing extraordinarily great sensitivity. Addition of small quantities of chemically inert substances to ES, which does not change its chemical structure, is capable of changing the sensitivity to mechanical influences to a significant degree. Finally, the sensitivity to shock can be changed by change of the test conditions. This is also impossible to explain by the direct influence of chemical structure.

At first sight it appears strange for chemical process to occur as a result of shock, which is an explosion, the decisive factor can be not the chemical forces, which connect the atoms into molecules, but the weaker forces of interaction between molecules, which determine the fluidity of the substance. However, this ambiguity is only apparent. The first stage of explosion upon mechanical influence is local heating, which results from friction, i.e., it depends on fluidity of ES. The influence of factors of chemical kinetics can appear only after that and only, inasmuch as primary heating occured. The development of a chemical process can play a decisive role only subsequently. In this very sense the intermolecular forces can have a determining significance on the appearance of explosion from shock.

Let us clarify what has been said by the following analogy. Let us imagine a cartridge of sensitive ES, lying on a shelf, located above a steel plate. If this cartridge is pushed from the shelf, then it will fall on the plate and explode. It is clear that the force, which it is necessary to apply, in order to shift the cartridge and to cause this explosion, is determined by the coefficient of friction between ES and shelf material, but not directly by the chemical structure of ES.

All this shows that the chemical structure of compound is by no means the only factor which determines its sensitivity. Not being able to consider quantitatively other factors, in examining of the question on the connection between the sensitivity and chemical structure we are forced to be limited by the accumulation, description and systematization of facts, which do not always produce an answer to the questions about the basic causes of various experimentally fixed regularities.

One of the first studies in this field was conducted by Kholevo, who established that despite the expectation weaker (in energy of explosion) xylyl and trinitromesitylene are much more sensitive to impact than trotyl (see Table 5.4).

A more detailed study of the sensitivity of different aromatic nitro compounds to impact was conducted by Wöhler and Wenzelberg. Their experiments (a 0.02 g sample of ES under pressure of 1000 a.t. was pressed into a brass primer cap and was closed from the top with foil) showed that the relationship found by Kholevo for methyl derivatives of trinitrobenzene may be applied to other substitutes, in nitro compounds of benzene. These authors conclude that shock sensitivity of explosive aromatic nitro derivatives is determined first of all by the total number of substituents entering the benzene ring. The type and the position of a substituent are not of great significance. Therefore, ES with different substitutes, but with the same total number of the latter possess approximately identical sensitivity to impact.

These conclusions are illustrated in Table 5.4, which shows the increase of sensitivity to shock with increase of the number of methyl groups, hydroxyls, halides and nitro groups on the benzene ring. The sensitivity is expressed in terms of work of the shock (energy of incident load after subtraction of the energy of recoil — see page 456), which is necessary to obtain 50% of explosions and referred to 1 cm^2 of the area of charge.

The data in Table 5.4 contradict to some extent the general considerations of factors which determine explosiveness and sensitivity. During introduction of energy wise "inert" substitutes, such as halides or methyl group, the sensitivity is increased just upon introduction of such substitutes, as NO_2, which increase the heat of explosion. However, it is first of all not known what are the thermal effects and speed of those reactions, which upon reaction to shock lead directly to explosions. Secondly, it is not known what determines the sensitivity and to what extent. Is it only the difference in chemical composition of the studies nitro compounds that plays the role or is it also the difference in their physico-mechanical properties (fluidity, melting point and others). Thus, it is not possible to give a reliable explanation of the observed phenomena.

Other attempts to establish the relationship between the chemical structure and the sensitivity of ES to shock were also unsuccessful, although they gave valuable factual information on the sensitivity of different ES, and also showed conditional nature of certain conclusions of Wöhler and Wenzelberg.

Thus, from the research of F. A. Baum, conducted in devices, different from those of Wöhler and Wenzelberg, different substitutes are by far not equivalent with respect to the character and the degree of their influence on the sensitivity of nitro derivatives of the aromatic series. Accumulation of electronegative substituents in nitro compound molecule leads, according to Baum, to loosening of the bond between atoms. The electropositive substitutes between two nitro groups, located in meta-position to each other, display an inverse effect.

In this fashion Baum explains the observed higher sensitivity of trinitro derivatives of phenols (picric acid, styphnic acid, trinitrophloroglucinol) as compared to sensitivity of trinitro derivative of corresponding methylbenzene (trotyl, xylyl, trinitromesitylene). Even greater influence is displayed by the amino group, which is more electropositive than methyl group (Table 5.5).

Introduction of amino group into the benzene ring leads to a very significant lowering of the sensitivity which is very apparent in the comparison of picric acid and trotyl with trinitroaniline and comparison of styphnic acid with trinitroaminophenol. The impact sensitivity of the investigated aromatic nitroamine — trinitroaniline and trinitrophenylene diamine — turned out to be so low that during test in standard apparatus and at standard height of drop of 25 cm, as well as at 50 cm (load 10 kg) in 25 experiments there were no explosions.

With increase of the number of CH_3 and OH groups the sensitivity of corresponding nitro compounds gradually increases. With increase of the number of NH_2-groups the sensitivity, on the contrary, drops.

Table 5.4. Impact Sensitivity of Nitro Derivatives with Different Number of Substituents (According to Wöhler and Wenzelberg)

Explosives	Number of substituents	Work of shock kg·m/cm²	Explosives	Number of substituents	Work of shock kg·m/cm²
Influence of CH_3-group:			Influence of Br atoms:		
Dinitrobenzene	2	19.5	Dinitrobenzene	2	19.5
Dinitrotoluene	3	18.9	Bromodinitrobenzene	3	13.9
Dinitroxylene	4	14.6	Dibromdinitrobenzene	4	12.5
Dinitromesitylene	5	13.8	Tribromodinitrobenzene	5	7.7
Trinitrobenzene	3	12.1	Influence of NO_2-group:		
Trinitrotoluene	4	11.4	Dinitrobenzene	2	19.5
Trinitroxylene	5	5.7	Trinitrobenzene	3	12.1
Trinitromesitylene	6	5.9	Dinitrotoluene	3	18.9
Influence of OH-group:			Trinitrotoluene	4	11.4
Dinitrobenzene	2	19.5	Dinitroxylene	4	14.6
Dinitrophenol	3	12.7	Trinitroxylene	5	5.7
Dinitroresorcinol	4	10.3	Dinitromesitylene	5	13.8
Trinitrobenzene	3	12.1	Trinitromesitylene	6	5.9
Trinitrophenol	4	8.2	Dinitrophenol	3	12.7
Trinitroresorcinon	5	4.0	Trinitrophenol	4	8.2
Influence of Cl atoms:			Dinitroresorcinol	4	10.3
Dinitrobenzene	2	19.5	Styphnic acid	5	4
Chlordinitrobenzene	3	12.0	Chlorodintrobenzene	3	12
Dichlordinitrobenzene	4	10.2	Chlorotrintrobenzene	4	11.3
Trinitrobenzene	3	12.1			
Chlorotrimtrobenzene	4	11.3			

Table 5.5. Impact Sensitivity of Different Trinitro Compounds of Aromatic Series (According to Baum)

Explosives	Frequency of explosions under standard conditions of test, in %	Energy of shock, at which the frequency of explosions constitutes 50%, kg·m/cm^2
α-trinitrotoluene	4	—
γ-trinitrotoluene	16	—
Trinitrophenol	18	2.40
Trinitroxylene	22	2.30
Trinitrocresol	34	2.14
Trinitroaminophenol	24	—
Styphnic acid	64	1.34
Trinitromesitylene	36	1.95
Trinitrophloroglucinol	100	—

On the basis of considerations of crystal lattice energies Baum also explains the difference in the impact sensitivity of azides of various metals. He calculated the relative magnitudes of the lattice energy of different azides and by comparing them with the frequency of explosions in tests with a drop hammer. He arrived at the conclusion that with decrease of this energy the sensitivity to impact increases. Since lattice energy is closely related to the energy of explosion, which in turn is an essential factor of explosiveness, the conclusion of Baum is well substantiated in principle.

For establishment the relationship between the structure of explosive organic compounds and sensitivity L. I. Bagal determined the impact sensitivity of a number of nitro derivatives of aromatic hydrocarbons with nitro group in the nucleus or in the lateral chain, nitrohalogen derivatives aromatic hydrocarbons, nitro derivatives of mono and polyatomic phenols, nitro derivatives of aromatic amines, aminophenols and carboxylic acids, aromatic azides, diazo compounds and their nitro derivatives. On the basis of the obtained results Bagal, just as Baum, arrived at a conclusion that the greater the number of weak bonds in the molecule, the higher will be the sensitivity of ES to impact. During the introduction of substituents into a molecule the sensitivity is affected not only by their nature, but also by the position, and the possibility of location in the plane of the benzene ring. In salts of aromatic diazo compounds, differing from all other nitro derivatives of the aromatic series, the nitro group lowers the sensitivity to impact, this influence is explained by Bagal through the ionic character of the considered compounds. The sensitivity to impact according to Bagal increases also in the case when there is a possibility of formation of intermolecular or intramolecular hydrogen bonds.

The general deficiency of the work of Baum and Bagel is the fact that they did not consider the influence of physical and mechanical, and to a certain extent the thermochemical factors on the sensitivity of studied compounds, which could be very significant.

2. Effect of Physical Characteristics of ES on Their Sensitivity

It was stated above that a large influence on the occurrence of explosion of ES upon impact is played by such characteristics as fluidity (coefficient of internal friction) and melting point. The effect of solid inert impurities at significant concentrations is determined first of all by the change of fluidity. Depending upon the properties of the substance and the conditions of impact the same impurity can increase or lower the sensitivity.

In this section we shall consider the influence of some other physical characteristics of ES, such as crystal size, aggregate state, polymorphism and temperature and density on the impact sensitivity. The influence of these characteristics is not always explained theoretically, and the considered relationship is primarily empirical in nature. It is necessary to add that a significant part of the corresponding research was conducted when even general concepts about the concrete mechanism for the excitation of explosion by impact were still absent. Therefore, the experiments were usually carried out without the calculation of those experimental conditions, which can play a decisive role.

Crystal sizes

Usually large crystals of ES were ascribed with an extraordinarily high sensitivity. Thus, Brunswig notes that with increase of crystal sizes of lead azide its impact sensitivity constantly increases, large crystals (3 mm long and 0.25 mm thick) explode in the moment of breakage or from contact with a feather, similarly to iodine azide. Meanwhile smaller crystals (0.1 mm in diameter) explode fron only the impact during drop of the load from a 65 mm height, and very fine crystalline powder when the height of drop is 200 mm. The high sensitivity of large crystals was supposedly explained by the increase of stresses, which in certain cases can lead even to spontaneous explosions.

The concept of highly increased sensitivity of ES in large crystals appeared as a result of works of Kholevo with azides, in particular with lead azide.

Hydrazoic acid and its salts were discovered in 1891 by Curtius. Soon after that the German Department of Defense conducted classified research for the purpose of practical use of azides. However, these experiments were accompanied by accidents and loss of human lives and were consequently ceased. Not knowning about this work, Wöhler started an analogous study, which was also accompanied by unexpected explosions, but it was completed successfully. Wöhler established that spontaneous explosions are observed only under definite conditions of crystallization, and namely, when big crystals are obtained. Having found appropriate conditions for crystallization, Wöhler achieved relative safety of the technological process for obtaining azide, ensuring its wide application.

Thus, the hypothesis on the exceptional danger of large crystals appeared. At present, the observations of Wöhler should be interpreted somewhat differently (see lower), and they cannot serve as the basis for solving the problem on the relationship between the magnitude of crystals and sensitivity to shock.

The fact that lead azide in large crystals does not necessarily possesses the prescribed state of exceptionally high sensitivity, may be seen from the following experiment. A big crystal of azide is placed between two soft steel disks (α-form). Upon the drop of load 10 kg in weight from a height of 50 cm the crystal was split into a fine powder, but there were no explosions, although the force of the impact was so great that on the surface of the upper disk in the place where crystal was located a dent was formed.

Other experimental data on the influence of crystal size on the sensitivity are quite contradictory in character.

Thus, in one of the later works Wöhler showed that between sample of lead azide with larger crystals (passing through sieve, having 400 holes per 1 cm^2, and are not passing through sieve with 1600 holes) and the sample of lead azide with small crystals (selected between sieves from 6400 to 10,000 holes per 1 cm^2) the difference in sensitivity to shock is not observed. Samples of mercury fulminate with short crystals (0.015 mm) and long (0.117 mm) also show identical sensitivity. The difference between macrocrystalline (passing through sieve with 169 and remaining on sieve with 400 holes per 1 cm^2) and the fine-crystalline material (passing through sieves with 6400 and remaining on sieve with 10,000 holes per 1 cm^2) examples of a series of nitro compounds was not observed (trotyl, picric acid, trinitrotrichlorbenzene, α-dinitrophenol).

On the other hand, there are also contrary data. Thus, Lenze established that fine-crystalline picric acid explodes when a 10 kg load is dropped on it from the height of 16 cm, while the macrocrystalline substance does not explode even when such load is dropped from the height of 20 cm. Conversely, in the case of nitroglycerine large crystals are significantly more sensitive than small ones. Thus, when a 2 kg load was dropped from the height of 20 cm on fine-crystalline nitroglycerine out of 10 experiments all 10 produced no explosions, whereas macrocrystalline nitroglycerine, under the same conditions produced 6 explosions out of 10.

The contradictory nature of data on the influence of crystal sizes on the sensitivity of ES to impact may be explained by the fact that experiments were conducted with different ES and in various instruments. At the same time for different ES this effect can appear to a different extent and at various intervals of crystal sizes. It is necessary to consider that in the case of large crystals the physical heterogeneity of ES, is larger. Furthermore, here it is possible also to have chemical heterogeneity: during slow crystallization, which is used for obtaining large crystals, impurity is disposed chiefly on their surface, which is the primary place of friction between crystals during shift. If the impurity is of high sensitivity, then it will increase the sensitivity of ES and visa verse.

For practical work with ES it is especially important to consider the possibility of the increased danger of handling highly sensitive ES in the form of big crystals. In view of the great sensitivity such ES are also dangerous and in the fine-crystalline state. If, however, the sensitivity is further increased at the expense of large dimensions of crystals, then these substances can become especially hazardous.

In the case of low sensitivity ES the influence of crystal size appears to a smaller extent, since upon strong blow, which is necessary for the excitation of explosion of such substances, large crystals will be fractured and the difference between samples with crystals of various dimensions will become small.

The presented data characterize the sensitivity to mechanical factors. Ya. I. Leytman established that with increase of degree of crushing of secondary ES their sensitivity to explosive impulse strongly increases.

In experiments the tested ES (1 g) was pressed in a shell under the pressure of 500 a.t., and over it was placed a lead azide charge. The completeness of explosion was judged from piercing of the lead plate, on which detonation took place. The minimum charge of lead azide was established, at which full explosion of secondary ES charge was obtained. These ES were used in two degrees of crushing: 1) ES, crushed to passage through sieve with 2500 holes per 1 cm^2 and the remaining in the sieve with 10,000 holes per 1 cm^2; 2) ES, obtained by precipitation with water or other solvent from acetone solution and completely passing through a sieve with 10,000 holes per 1 cm^2

(particle size of 1-4 μ).

Table 5.6 gives basic results for trinitro compounds with one, two and three substitutes.

Table. Sensitivity of ES to Explosive Impulse as a Function of the Degree of Crushing

Explosives	Minimum charge of lead azide in g	
	Moderate crushing	Strong crushing
Trinitrobenzene	0.19	0.06
Trinitrochlorobenzene	0.14	0.05
Trinitroaniline	0.13	0.05
Trinitrotoluene	0.10	0.04
Trinitrobenzoic acid	0.10	0.04
Trinitrophenol	0.08	0.03
Trinitrobenzaldehyde	0.05	0.02
Trinitromethaxylol	0.34	0.08
Trinitromesitylene	0.43	0.13
Styphnic acid	0.04	0.02
Trinitrophloroglucinol	0.04	0.02
Trinitrodichlorobenzene	0.18	0.06
Trinitrotrichlorbenzene	From 1 g incomplete detonation	0.29

From the data of Table 5.6 it is clear that the increase of the degree of crushing,* within the investigated limits, decreases the minimum charge of the initiator, which is necessary to produce an explosion 2-4 times. The sensitivity of trinitro compounds, containing different substituents, is affected by the nature and the number of substituents.

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*Certain influence on the results of experiments could be caused by the difference of charge density, inasmuch as compressibility of moderately and finely crushed powders is not identical and at the same pressure (500a.t.) the attained density could have been different.

Aggregate state

The problem of the influence of the aggregate state on the sensitivity of ES has been investigated very little. At the same time this question presents not only a theoretical, but also some practical interest. Soon after the beginning of broad application of nitroglycerine explosives in the Western Europe it was observed that in the winter the number of accidents increases. Since dynamite can freeze in the winter (melting point of nitroglycerine is +13°C), then the increase of the number of explosions might be explained by the increased sensitivity of frozen dynamite. Despite this assumption the laboratory research showed that frozen nitroglycerine and dynamite are less sensitive than unfrozen. Thus, according to Ville liquid nitroglycerine explodes when 1 kg load is dropped from a height of 10 cm, while frozen — only when the height of the drop is 40 cm. In exactly the same way unfrozen and frozen guhr dynamite explodes at the height of drop of 2 kg load of 7 and 20 cm respectively. In addition to the test on a drop hammer Ville conducted a number of tests with frozen dynamite, corresponding to real situations during transportation and use of dynamite: throwing of boxes containing 5, 10, 15 and 25 kg guhr dynamite or dynamite gelatin on rocks from a height of 10 m, fast driving of nails into frozen dynamite, sharp fracturing of shells, etc. Not one of these experiments produced an explosion.

The contradiction between the results of laboratory research and practical experiment, might be explained by the difference of conditions of freezing in both cases, and in sensitivity of frozen nitroglycerine associated with this difference.

Table 5.7 gives comparative data on the sensitivity of liquid and solid nitroglycerine under different conditions. All experiments were carried out at the same temperature of +5°C. The blow was produced by a load of 2 kg from a height of 20 cm.

As can be seen from the Table 5.7, freezing of nitroglycerine does not necessarily lead to the decrease of its sensitivity. A great influence on sensitivity is played by the temperature, at which crystallization of nitroglycerine occurred. At high temperature (+10°C) nitroglycerine froze slowly, in addition then big crystals with high sensitivity were formed; at low temperature (-11°C) small crystals with relatively low sensitivity were obtained.

Table 5.7. Sensitivity of Nitroglycerine to Impact Under Different Conditions of Freezing

State of nitroglycerine	Temperature of freezing in °C	Number of explosions out of 10 experiments
Frozen nitroglycerine	-11	0
The same	0	2
The same	+10	6
Liquid nitroglycerine	—	4

The test of 93% blasting gelatin showed that the temperature of freezing does not produce any noticeable influence on its sensitivity. However, such influence can appear if dynamite exudes.* Therefore, the cause of the increased sensitivity of frozen dynamite may be found in freezing it at relatively high temperature and also in the exuding state.

It is necessary to keep in mind also the fact that under practical conditions the mechanical effect in the case of unfrozen dynamite are weakened due to its plasticity, while the frozen

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*The excretion of drops of liquid nitroglycerine from dynamite is called exudation.

dynamite is hard and no longer absorbs the shock. Under the conditions of the usual laboratory tests for impact sensitivity this distinction is not apparent. However, if one were to compare the sensitivity of frozen and unfrozen dynamite otherwise, for instance by dropping a ball of dynamite, about 100 g in weight, on to a steel plate, then the influence of the aggregate state is distinctly observed; frozen dynamite turns out to be more sensitive and explodes at a height of drop of 7.5 m, whereas the unfrozen dynamite under such conditions produces no explosion.

According to American investigators, the sensitivity of trotyl, in a closed volume, strongly increases during the transition from a solid state to liquid (Table 5.8). In these experiments the measure of sensitivity was considered the minimum height of 2 kg load, H, at which under certain conditions one obtains at least one explosion from ten experiments.

Thus, the available data on nitroglycerin do not permit us to answer the question of which aggregate state is more sensitive. Since the sensitivity of solid nitroglycerin can be changed within very broad limits by the change of the temperature of freezing (dimension of crystals); trotyl in the liquid state has a higher sensitivity.

Table 5.8. Sensitivity of Trotyl to Impact at Various Temperatures

Temperature °C	State of trotyl	Height of drop, H, of load cm
-40	Solid	46
20	Solid	36
80	Liquid	18
90	Liquid	8
105-110	Liquid	5

From the theoretical considerations, the change of the state of aggregation can affect sensitivity since it strongly changes the fluidity of the substance. However, the relationship of the change of fluidity and sensitivity is not simple. Thus, during transition from solid state to liquid, the sensitivity can be increased or decreased depending on the conditions, under which the test is conducted. If the change of fluidity approaches the optimum conditions for the appearance of local heating, then the sensitivity will be increased and visa verse.

Polomorphous form

Many ES, for instance azides of lead and mercury, nitroglycerin diglycoldinitrate, dyne, octogene, hexogene, trinitobenzene, trinitrotoluene and others, can exist in different crystalline modifications. The study of explosive properties, in particular, the sensitivity of different modifications, conducted for certain ES showed a significant difference between them.

Thus, for nitroglycerine the stable modification crystallizes in the rhombic system, and it possesses a noticeably greater sensitivity than the labile form, which crystallizes in triclinic system. With 2 kg load the first of these gives 50% of explosions at the height of drop of 15-20 cm, and the second modification at the height of 20-30 cm. In the case of primer, the labile form is also less sensitive, although here the important role is played by the conditions of freezing.

In 1931 Miles described two forms of lead azide α-form — stable and β-form — unstable.

α-azide is orthorhombic. The density of its crystals constitutes 4.71 g/cm^3.

α-azide is obtained under the usual conditions of deposition. It may be obtained in large crystals by slow crystallization of azide, dissolved in 15% solution of potassium acetate. The β-modification is monoclinic, in the form of needles, has a density of 4.93 g/cm^3 and is obtained during slow diffusion of solutions of sodium azide and lead salt toward each other.

For both modifications Miles obtained 3 cm in length and more, where, these crystals by no means possessed in the dry form, the extraordinarily high sensitivity ascribed to them. During work on the production of these modifications Miles established a very curious phenomenon; very frequent in obtaining β-form during crystallization the azide spontaneously explodes.* This inclination of β-azide to spontaneous explosions can not be explained by its law stability, since dry crystals do not give such explosions and can be kept for years, without being changed. Although β-crystals are somewhat more sensitive to shock and heat as compared with α-form, the difference between them is not too great.

In view of the research of Miles the real cause of accidents, taking place during the first experiments on production of lead azide, were probably small crystals, as was assumed earlier, and the formation of β-form of the unknown at that time, which lead to spontaneous explosions.

For crystals of β-azide of mercury, HgN_6, the tendency to explode during crystallization is even more pronounced, where they are sensitive even in the dry form. Spontaneous explosions of mercury azide were observed not only during formation of crystals from

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*Explosions sometimes occur with large crystals of the α-form of lead azide.

solutions, but also under conditions. Thus, in one experiment, in which crystals of α-azide of mercury were decomposed in the test tube in vacuum and a certain fraction of it was distilled and condensed in the cold part of the instrument. The explosion occurred after the removal of the furnace from the test tube, i.e., during cooling of ES. An analogous phenomenon was described by Mürauer. He heated mercury azide in a vacuum with the aid of a wire, heated by the passage of current. During heating mercury azide did not explode, but disappeared in the form of gases, liberated at the expense of decomposition. Around the wire a hollow shell of azide was formed, partially fused on the inner side. After turning off the current, sometimes with a delay up to 30 sec, detonation occurred. Mürauer considers that the cause of the explosion is the cracking of the alloyed mass during cooling.

For other investigated azides (silver and mercurous oxide) the existence of modifications was not revealed.

For octogene according to the American data there exist four polymorphous forms, greatly differing in their sensitivity to impact.

Temperature

According to Kronkvist, to excite an explosion of a drop of nitroglycerine, placed between steel plates, at 15°C, it is necessary to produce the energy of blow of 0.8 kg-m, at 30° the energy must be 0.6-0.7 kg-m. From the experiments of other researchers, nitroglycerine under somewhat different conditions explodes at 16°C, when the energy of the blow constitutes 0.2 kg-m, at 94°– 0.1 kg-m, and at 182° for excitation of the explosion it is sufficient to produce only the lightest shock.

The increase of sensitivity of dynamite gelatin to shock as a function of temperature is expressed, according to Ville by a curve shown in Fig. 5.9.

According to the data of Taylor and Weale, the sensitivity of fulminating mercury increases with temperature somewhat differently (see Fig. 5.3). This dependence may be expressed by formula

$$BK + Ae^{-E/RT} = k, \qquad (5.10)$$

where K is the work of impact;

k, B, A, E are constant, and the other letters have their usual meaning.

It is interesting to note that for mercury fulminate the magnitude of E, determined from the experimental data and the expression (5.10), turned out to be of the same order (16.8 kcal), as the energy of activation of slow thermal decomposition.

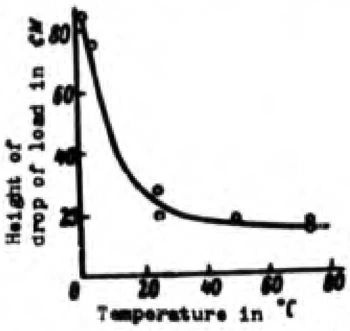

Fig. 5.9. Change of sensitivity of dynamite gelatin to shock as a function of temperature (according to Ville). The height of drop of 2 kg load, from which explosions begin to occur.

A study was also made of the influence of temperature on the sensitivity to explosive impulse, for which the limiting charge of mercury fulminate at normal temperature and at -110°C was established. In the first case the minimum charge for pyroxylin, picric acid and cheddite was 0.25 g, and for blasting gelatin — less than this magnitude. At -110°C the limiting charge for blasting gelatin was increased to 1 g, while the remaining ES did not detonate even when the charge of mercury fulminate was 2 g. Thus, with the lowering of temperature the sensitivity was significantly lowered to the explosive impulse. In evaluating these data it follows, that they reflect not only the decrease of the sensitivity with lowering of temperature, but also possibly on the effect of the temperature on the initiating action of mercury fulminate.

In all given examples ES appeared to be more sensitive at higher temperature. One would expect this, since increase of the initial temperature decreases the quantity of heat necessary for heating ES to such a temperature, at which a center of burning can occur. It is necessary, however, to consider that the change of initial temperature also changes the fluidity of ES. If the fluidity is changed so that conditions of formation of the center of local heating upon impact become less favorable, then the appearance of the explosion can be hampered and the sensitivity will become lower.

Vasil'yev in the laboratory of Kholevo established that during the test in instrument No. 1 with a definite charge of trotyl the maximum frequency of explosions is observed at room temperature, with decrease and increase of temperature the frequency drops. For viscous ES, PETN, hexogene and trinitromesitylene with increase of temperature, starting from -100°C, the frequency of explosions increases and its maximum lies near the melting point. Conversely, in the instrument No. 2 for PETN, hexogene and trinitromesitylene the frequency of explosions with increase of temperature from -100°C up decreases.

Density

According to Taylor and Weale, with the increase of density the sensitivity of powdered ES to shock decreased. With respect to primer, as we have seen, with increase of density of charge all ES show decrease of sensitivity. In exactly the same way the increase of the density of a passive charge decreases distance of the transmission of detonation (at constant density of the active charge).

§ 3. Experimental Methods for the Evaluation of the Sensitivity of ES and the Effectiveness of the Initial Impulse

1. The Sensitivity of ES to Mechanical Influences

Sensitivity to shock

The determination of sensitivity to shock are usually based on the fact that, the load is dropped from certain height on the explosive, placed on an anvil. The larger the height of drop and the weight of the load, at which the explosion still does not occur, the lesser is the sensitivity of tested ES.

Some researchers take not the height of drop of load, but difference between this height and height of the recoil of the load after the shock as the characteristic of sensitivity, motivating this by the fact that the shown difference is the measure of energy, absorbed during the shock. Besides on the basis of the assumption that part of the energy is expended for the residual deformation of the system – impactor – ES - anvil, determines the occurrence of explosion. However, during the explosion from a shock not only the energy expended on permanent deformation is essential, but also the energy of elastic deformation of the system, since the pressure, under which ES exists during the blow, affects the magnitude of the internal friction coefficient, and also the development of the initial center of reaction, in particular, the transition of the initiated burning into explosion. Furthermore, in general it is difficult to establish, how is the energy distributed among individual parts of the system, participating in the blow, and what fraction of it determines the appearance of the centers of heating in ES. Therefore, there are no sufficient basis for the use of the difference between the height of drop and the height of rebound of load instead of the height (work) of drop of the load.

The sensitivity of various ES can be greatly different. Due to this during a test with the same load it would be necessary to use either a very high drop hammer, or a very low altitude of the drop. Therefore, one usually works with different loads. A question arises on, how is one to compare the results of such determinations. It would have been possible to expect that the impact of a small load with identical energy will be more effective with respect to the excitation of the explosion than the blow of large load, since the speed of drop of the load at the moment of the blow, and consequently also sharpness of blow, is larger in the former case. On the other hand, at a high speed of drop of load the duration of blow is less and the occurrence of centers of explosion may not be developed. Which one of the indicated factors will predominate in every specific case, it is difficult to estimate quantitatively. Certain studies (Table 5.9) show that influence of the speed of the drop of the load (at least during small changes of speed) is not apparent and that it is possible to take the total energy of blow as characteristic of sensitivity (i.e., the product of weight of load and the height of its drop).

However, in other works there was observed a dependence of the energy of blow, necessary for excitation of explosion, on height of the drop of the load. Thus, according to Kennen and others (see Appendix 3), with the increase of the height of drop of the load the energy of the blow, at which explosions were observed, decreased significantly.

If one gradually, increases the height of the load drop by let us say 1 cm and at every height one conducts a definite number of experiments (for instance ten), then at small heights all ten experiments will give rejections, after which one will obtain one explosion from ten, then two, three etc and at last all ten experiments will give an explosion. Here, frequently the interval of heights of drop of load — from a height at which there are no explosions to a height at which all experiments give explosion, is significant.

Table 5.9. Effectiveness of Blow as a Function of the Weight of the Load (According to Taylor and Weale)

Weight of the falling load G in g	Mercury fulminate		Composition with lead styphnate	
	Critical* height of drop H, cm	Product GH, g-cm	Critical height of drop H, cm	Product GH, g-cm
14	35.6	500	45.7	640
28	18.0	500	22.9	640
57	8.9	500	11.9	680
85	5.8	495	7.9	670
113	4.3	485	5.8	655

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*The height of drop, at which one obtains 50% explosions and 50% rejections.

In this respect the determination of the sensitivity to impact differs from the determination of the temperature of the flash, at which the transition from 0% flashes to 100% occurs in a relatively small temperature interval.

In connection with the indefinite nature of the boundary between the height of drop of the load, leading to rejection in all experiments, to the height of drop which produces explosions in all experiments, a question rises as to what height of drop of load one should consider as characteristic of the sensitivity of ES?.

This question in various countries and in different research establishments was resolved in different ways.

In the Bureau of Mines of the United States and in Germany at every height of drop of the load 6 (sometimes 10) experiments are conducted. For a given ES they consider characteristic the maximum height of drop of load, at which one obtains no explosions. For establishment of this height, naturally, it is necessary to determine also the nearest height, at which one obtains at least one explosion from six experiments. The same method is used according to the All-Union Government Standard 4545-48 to test industrial ES, using a 2 kg load and determining the minimum height of the drop of the load from 6 experiments.

For ES of different designation, according to the All-Union Government Standard 4545-48, 25 experiments are conducted at constant height and load (usually 25 cm and 10 kg) and the percent of explosions is established which serves as a comparative characteristic of sensitivity.

This method of evaluation of the sensitivity of ES is the most wide-spread in our scientific research establishments, although it is not necessarily the most expedient and accurate, especially in those cases, when the percent of explosions is near to zero or near to 100%.

At last, it is possible to determine the whole curve, which gives the percent of explosions, as a function of height of drop, but this method requires large number of experiments and, furthermore, it is still unclear what point of the curve one should take as characteristic of the sensitivity of ES.

F. F. Yakovlev and B. L. Kondratskiy tried to give an answer to this question through the following reasoning.

Let us assume that the variation of the results, at the same height of drop of the load one obtains explosions and rejections, is caused by the random influences, such as for instance, heterogeneity of the sample and its distribution on anvil, the possibility of misalignment during drop of load, etc. If one were to picture an ideal impact hammer on which all these influences are excluded, then on this instrument we should obtain some critical height, below which we shall have 100% rejections, and higher – 100% explosions. Let us imagine now that after the establishment of the critical height the ideal drop hammer became real, i.e., all random effects became operative. It is obvious that inasmuch as these effects are random, they will act in equal number in favor and against the explosions. Therefore, when the height of drop of the load, producing on ideal drop hammer 100% explosions is found, we will now obtain 50% explosions and 50% rejections. In other words, working on a real drop hammer and establishing the height, corresponding 50% explosions, we will define as an "ideal" critical height, which is the most appropriate characteristic of the sensitivity of tested ES.

It is necessary to note that the above reasoning assumes the random nature of influences, which determine the result of the experiment on the drop hammer. Such an assumption requires confirmation. In one of the English works the investigators compared the experimental curve for the frequency of explosions of highly sensitive infusible ES as a function of the height with the theoretical curve, obtained from the Gaussian distribution law. All of the experimental points fell well along the theoretical curve, which confirms the assumption that this phenomenon obeys the random distribution law.

In other studies for other ES, the obtained distribution curves differ greatly from the curve, calculated on the basis of the probability law. Kholevo explained these deviations. He showed that the energy of impact, giving rise to 50% explosions, can not be taken as the true measure of the sensitivity of ES, since the occurrence of the explosion is determined not simply by the magnitude of this energy, but is a more complex function.

The reasoning of Yakovlev and Kondratskiy is correct in principle only for the case, when the characteristic of effectiveness of impact is that parameter, which directly determines the production of local heating (the rate of absorption of energy). Unfortunately, the quantitative determination of this characteristic is not realized in practice. Therefore, we are forced to use the energy of impact as the index of effectiveness. In this case, i.e., if one were to characterize the sensitivity of ES to impact in terms of the work (height of drop) of load, which produces a definite number of explosions, if the frequency of explosions increases regularly with height and approaches unity, it is convenient to take 50% as a characteristic measure. The recent works are usually making use of this characteristic.

Experimental methods for the determination of the sensitivity to impact are sufficiently developed with respect to the construction of impact hammers. Our most widely used impactor was developed by Kast, for determination of the sensitivity of primer ES use is made of a drop hammer developed by Wöhler. The instrument of Kast (Fig. 5.10) consists of massive anvil, mounted on foundation, and two guide rails between which the load which impacts the change is sliding freely. The load is secured at the desired height by means of a clamp, attached to the descension device. This hammer has an arrangement for catching the load after the rebound. The V. S. Kozlov modification of the Kast impactor is shown in Fig. 5.11.

If ES is placed directly on the anvil, then it is difficult to ensure the constancy of the thickness of ES layer as well as the area, over which the energy of impact is distributed. It is also difficult to insure the parallelism of surfaces of the impactor and the anvil. Therefore, the ES samples (0.02-0.05 g) are usually placed in a special stamping device (see Fig. 5.4), which is centered on the anvil by means of a metal brace. For pistons roller bearings are used, characterized by the high degree of constancy of the mechanical properties and accuracy of the dimensions.

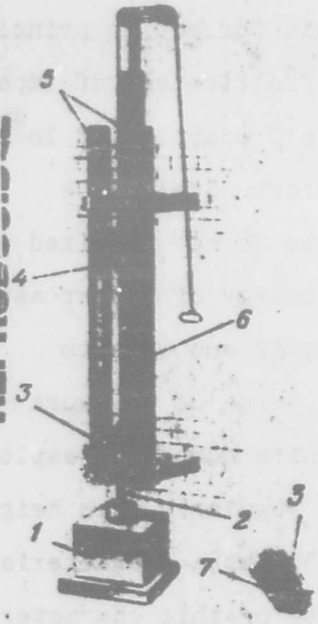

Fig. 5.10. Kast design of impactor for determination of the impact sensitivity of the secondary ES. 1) anvil; 2) stamping device; 3) load; 4) load clamp; 5) guide rail; 6) toothed rod; 7) tooth for catching the load on the rod during rebound.

In the stamping device the possibility of misalignment of the piston during impact is reduced to a minimum. The area of impact and the thickness of ES layer are constant, and the reproducibility of experimental results is much better than in the case of test without the stamping device.

The stamping devices exist basically in two variations (see Fig. 5.4a and b). If in device No. 1 the roller is accurately fitted to the bore and has no rough faces, then during impact viscous ES will only be compressed, and will not leak out. If, at the same time, the ES does not contain any air bubbles, then heating and consequently explosion will not occur, even if for the excitation of explosion of a given ES only slight heating is required, which may be easily obtained during friction. In order to detect the high sensitivity of ES under conditions of its flow, one should also conduct tests in the device No. 2, which differs by the presence of a groove in the casing at the level of the location of ES. Experiments show that viscous ES, which do not explode in device No. 1 can, with all other things being equal, produce a high frequency of explosions in device No. 2 and in the corresponding conditions of practical use.

The device used by the All-Union Government Standard 2065-43 (see Fig. 5.4c) is something intermediate between the device No. 1 and the device No. 2. Rollers of the standard device have faces, which form a radial clearance, which to a certain extent plays the role of the groove in the device No. 2.

During tests on the Kast's impactor one uses loads from 2 to 20 kg depending on the sensitivity of ES. In view of the poor reproducibility of the results, the impact sensitivity tests are conducted, as a rule, in parallel to the standard ES, which are close in sensitivity to the tested substances (trotyl, tetryl, pyroxylin etc). It is also recommended to conduct tests by the "variable impact" method, alternating the experiments with the unknown and the standard ES. Such a method tends to eliminate the influence of those uncontrollable changes of experimental conditions, which can take place in the course of every series of tests.

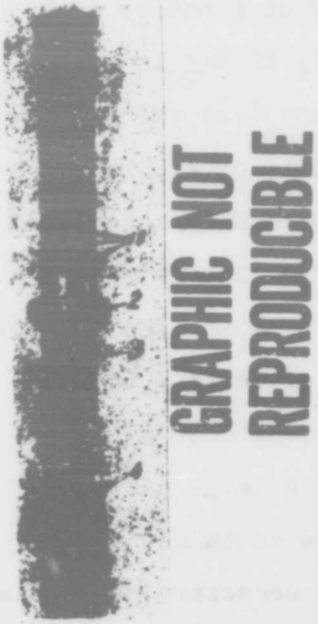

Fig. 5.11. Kozlov's design impactor. 1) guides; 2) load clamp; 3) load; 4) anvil.

For the determination of the sensitivity of primary ES one normally uses the Wöhler impactor, the construction of which may be seen on Fig. 5.12. The tested primary ES (0.02 g) is pressed into a brass primer cap and covered by a circle of copper foil. Five experiments are conducted at every position of the pendulum. Normally during tests one establishes the so-called <u>upper and lower sensitivity limits</u>. The first of the limits corresponds to the minimum height at which all five experiments give explosions, and the second limit corresponds to the maximum height at which all experiments give rejections.

The characteristics of the impact sensitivity of a number of ES are given in Tables 5.10 and 5.11 for the secondary ES and in Tables 5.12 and 5.13 – for the primary ES. Tables 5.10 and 5.12 are compiled according to the data of Kistiakowsky in an American book: Encyclopedia of Chemical Technology. In one of the recent works on the impact sensitivity of ES and methods of testing the most complete summary of data is given on the sensitivity of a large number of ES. These data are contained in Appendix 3. It is necessary to stress again that the data of all tables with respect to the absolute values of given quantities as well as with respect to their relative values are very conditional in nature. This results from the fact that the sensitivity depends strongly on many conditions of impact, which for various researchers, just as in practice, are not identical. This peculiarity of the sensitivity of

Fig. 5.12. Wöhler impactor. 1) lead; 2) ejector; 3) stand with a capsule, striker and a protective clamp.

ES to mechanical factors, discovered and explained in the works of Kholevo is of great practical significance. The establishment of a low sensitivity of ES by some one method, for instance by the All-Union Government Standard 4545-48, does not mean that under different conditions, which can take place in practice, the absolute and the relative sensitivity of this ES will not appear much larger and will not lead to an explosion. Therefore, to evaluate the danger of ES in production and in use it is especially important to determine the sensitivity under different conditions, as close as possible to those conditions of mechanical influences, which are encountered in practical work. These conditions vary, and they can not always be reproduced in the laboratory. As simple examples one might list splitting, drilling, treatment of the surface of charge, drilling of ES charge in a blast hole etc. These and similar tests under stressed conditions in comparison to other technologically known ES, can yield information regarding the permissible intensity of different treatment and stresses of the new ES, for which direct industrial experimental data are not available.

Table 5.10. The Impact Sensitivity of the Secondary ES According to the Tests by the Method of the U. S. Bureau of Mines*

ES	Trinitrobenzene	Trinitrotoluene	Picric acid	Ammonium picrate	Tetryl	Hexyl
Height of drop of load, H_{min} cm	46	100	82	100 do not explode	26	27

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*During the tests the minimum height was established, at which at least one explosion was obtained in ten experiments. ES samples (0.02 g) were placed on the steel anvil in the layer in the form of a circcle, about 1 cm in diameter. The impact of load (2 kg) was transmitted to ES through a piston, the tip of which (1 cm diameter) was preliminarily pressed against the surface of ES.

Table 5.10 Continued

ES	Nitroguanidine	Hexogene	Octogene	Ethylene dinitroamine	Tetranitromethane	PETN
Height of drop of load, H_{min} cm	47	18	32	43	100 do not explode	17
ES	Dipentaerythrite Hexanitrate	Erythritol Tetranitrate	Hexanitromannite	Nitroglycol	Dinitrodiglycol	Nitroglycerine
Height of drop of load, H_{min} cm	14	10	8	56	100 do not explode	15

Table 5.11. The Impact Sensitivity of Certain Secondary ES*

ES	Frequency of Explosions %
Trotyl	4-8
Amatols	20-30
Picric Acid	24-32
Tetryl	50-60
Hexogene	70-80
PETN	100
Smokeless Powder	70-80

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*10 kg load, height of drop — 25 cm; the test was conducted in pressing devices according to the All-Union Government Standard 2065-43.

Table 5.12. The Impact Sensitivity of Primary ES

ES	Mercury fulminate	Lead azide (with dextrin)	Silver azide	Diazodinitrophenol	Lead styphnate	Lead dinitroresorcinate	Nitrogen sulfide
Height of drop of load* H_{min} cm	5	11	6	5	8	68	20

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*Minimum height of drop of 2 kg load, at which at least one explosion appears from ten experiments.

Table 5.13. The Shock Sensitivity of Certain Primary ES According to Tests on the Wöhler Impactor (the Diameter of Striker is 1.5 mm)

ES	Weight of load kg	Height of drop of load, at which five explosions and five rejections were obtained, cm
Mercury fulminate	0.69	8.5/5.5
Tetrazene	0.69	12.5/7
Lead azide	0.98	25/7
Lead styphnate	1.43	25/14

Sensitivity to friction (slipping blow)

As we have seen, that explosion which occurs as a result of impact is usually caused by friction, to which is subjected the compressed and the fluid ES. However, the sensitivity to friction is not identical with the sensitivity to impact. On the one hand, the expiration of ES during impact occurs, as a rule, under more or less high pressure. This reflects also on the internal friction coefficient of ES and especially on the development of ignition. On the other hand, ES can be so viscous that it will not flow not only in device No. 1, but not even in device No. 2. In such a case the high sensitivity to friction, if it is characteristic of the tested ES, will not be apparent during the test for the impact sensitivity. In order to reveal this sensitivity and thus to characterize more fully those conditions of mechanical influences, under which ES may be dangerous, the test for impact sensitivity in the devices No. 1 and 2 must be supplemented by tests for the sensitivity to friction or, more exactly to the slipping blow.

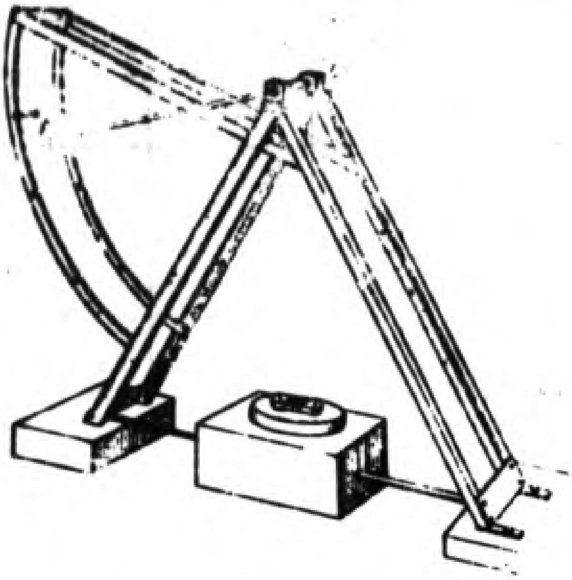

Fig. 5.13. Frictional pendulum for the determination of friction sensitivity of ES.

In literature there is a description of the three basic methods for the determination of the sensitivity of ES to friction: 1) with the aid of a friction pendulum (U. S. Bureau of Mines method); 2) grinding in a porcelain mortar and 3) on the Bouden-Kozlov instrument.

The friction pendulum consists of steel anvil, on which the tested ES (7 g) is placed and a pendulum 185 cm in length in the form of a durable steel rod, strengthened on its end by a shoe (Fig. 5.13). In the case of necessity it is possible to mount on additional load on the shoe. On the anvil there are three transverse grooves, in which the ES is retained during the passage of the shoe of pendulum above it. There are two forms of shoes: steel and steel covered with hard fiber. The test consists of the pendulum shoe, lifted and secured by a holder at a definite height is lowered with the aid of a cord. During the passage of the pendulum shoe above the anvil the ES is subjected to friction between the surface of the anvil and the surface of the shoe. The frictional force may be regulated by changing the height of the rise of the pendulum, the weight of additional load and the use of shoes with friction surfaces made of different materials. ES is considered to have passed the test for mining use, if in ten experiments with hard fiber, shoe, additional load of 20 kg and the height of rise of load – 1.5 m it does not produce an explosion, or burning, or any distinct crackling. For preservation of the fiber surface, which is rapidly destroyed in such experiments, the tests are started with stabler steel shoes. If in ten experiments an explosion does not occur, then the test is considered finished. Otherwise the test is conducted with a fiber surface shoe. The result of such a test is final. The results of the comparative test of certain individual ES by this method with a steel shoe are given in Table 5.14.

Table 5.14. Sensitivity of ES to Friction from the Test Data on Frictional Pendulum

ES	Dinitrobenzene	Trinitrobenzene	Trinitrotoluene	Ammonium picrate	Tetryl	Hexyl
Number of explosions out of ten experiments	0	0	0	0	0	0
ES	Nitroguanidine	Hexogene	Octogene	Ethyldinitramine	Tetranitromethane	PETN
Number of explosions out of ten experiments	0	2	2	0	2	5
ES	Dipentaerythrite hexanitrate	Nitroglycol	Dinitroglycol	Nitroglycerine		
Number of explosions out of ten experiments	10	7	10	10		

According to the second method the sensitivity to friction is determined by grinding 0.05 g of ES in an unglazed porcelain mortar with an unglazed pistil. It is understood that such tests are qualitative and very subjective in character. The results of tests of different ES by this method are given (according to Kast) in Table 5.15.

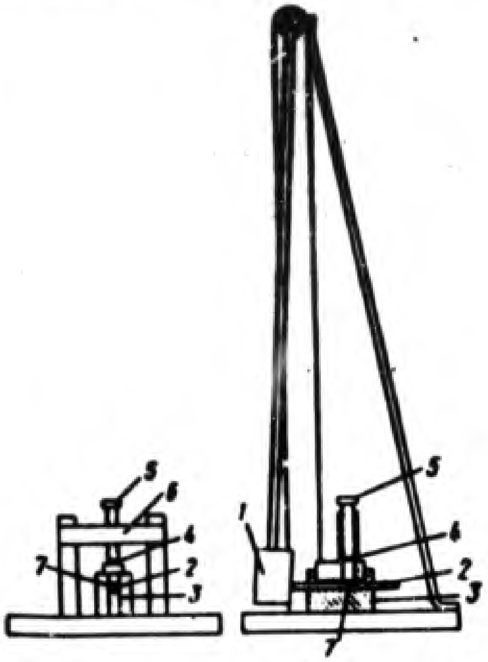

Fig. 5.14. Bowden's instrument for the determination of the sensitivity of ES to friction. 1) pendulum load; 2) right-angle steel rod; 3) motionless steel block; 4) steel roller; 5) pressure bolt; 6) cross beam; 7) ES.

Bowden and Horton developed an instrument for the determination of the sensitivity of ES to friction. It is shown schematically in Fig. 5.14.

During tests on this instrument a film of ES is placed on the upper surface of the right-angular rod 2 and is press to the rod by means of a steel roller 4. Tightening bolt 5 can produce the necessary pressure on ES. This pressure can be determined either by measurement of the flexure of the cross beam 6, or a lever may be used.

The load of the pendulum 1 is lifted to a definite height and then permitted to fall and strike rod 2, which slips along the lubricated surface of the motionless block 3. Thus, ES is subjected to a rapid shift.

V. S. Kozlov modified this instrument. First, he used a hydraulic press to apply the pressure on ES and secondly, he changed the device for placement of ES (Fig. 5.15). A specimen of ES is compressed between two rollers, 10 mm in diameter. The pendulum impact is transmitted to the upper mobile roller 1, which shifts between the above located stationary support 2 and the lower roller 3, secured in a sleeve 6. The deficiency of this variation of the instrument is the fact that the resisting force may be not identical on the faces of the travelling roller 1. On the upper face it is determined by the friction coefficient of steel against steel, but on the lower face it is a function of the internal friction of ES or the external friction coefficient of ES against steel. Due to this a certain misalignment of the roller usually takes place during the impact. Actually during tests in this type of instrument we may deal not with friction, but with a combination of friction and the impact of the edge of the upper roller 1 against the face of the lower roller 3.

Table 5.15. Sensitivity of Different ES to Friction According to Tests in a Porcelain Mortar

ES	Behavior of ES during grinding
Black powder	Does not react
Pyroxylin	The same
Trotyl	The same
Ammonite	The same
Picric acid	Produces a weak burning odor
Tetryl	Produces weak crackling
Gelatin dynamite	Explosion
Cheddite	The same
Lead picrate	The same

The change of the frequency of explosions in the case of the constant energy of impact of the pendulum as a function of pressure for a number of ES is shown in Fig. 5.16.

The characteristic of sensitivity in this test can be the pressure at which one obtains 50% or some other definite frequency of explosions.

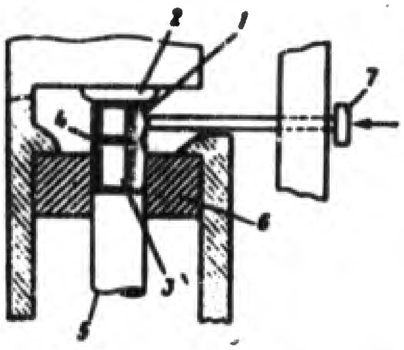

Fig. 5.15. A section of the Bowden-Kozlov instrument for determination of the friction sensitivity of ES. 1) mobile roller; 2) support; 3) stationary roller; 4) ES; 5) piston for transmission of pressure from the press to the roller 3; 6) sleeve; 7) rod with head, which transmits the impact.

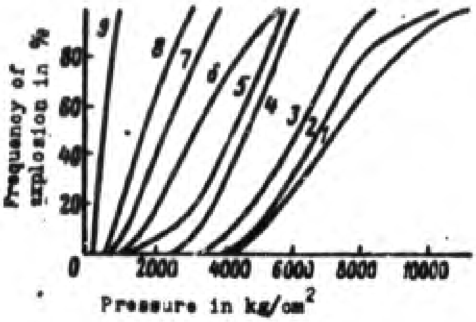

Fig. 5.16. Change of the frequency of explosions as a function of pressure during the test of ES for sensitivity to friction of according to Kozlov's method. 1) trotyl; 2) dinitronapthalene; 3) trinitrobenzene; 4) tetryl; 5) hexogene; 6) PETN; 7) pyroxylin; 8) lead azide; 9) mercury fulminate.

Sensitivity to being shot through by a bullet

The explosives which are used for military purposes are usually subjected to tests for sensitivity to being shot by a bullet. In one variation this test is executed as follows. A piece of cast-iron pipe 5 cm in diameter and 5 cm in length is filled with the tested ES, closed on both sides with threaded covers and shot through from a rifle from a distance of 9 m (taking the necessary precautions against fragments).

Table 5.16 gives results of tests of certain ES by this method.

Byurlo studied the factors, which determine the occurrence of detonation when bullets pierce ES packed in wooden crates. He established that picric acid detonates if the speed of bullet* at the time of impact exceeds 400 m/sec. To detonate granulated pyroxylin powder the speed of the bullet should be not less 1100 m/sec. The

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*A stone ball weighing about 4 g, was used as bullet.

remaining secondary ES occupy intermediate positions with respect to the speed of the bullet, which is necessary to produce detonation. Bullets with a flat tip produce detonation easier than conical bullets. The initiating ability increases with increase of the weight of the bullet if its velocity is maintained constant.

Table 5.16. Results of Tests of ES for Sensitivity to being Shot Through by a Bullet

ES	Trotyl	Picric acid	Ammonium picrate	Tetryl	Hexyl	Nitroguanidine
Number of explosions from 10 experiments	0.5	5	1	7	0	0
ES	Ethylenedinitramine	Hexogene	PETN	Nitroglycerine	Ammonium nitrate	
Number of explosions from 10 experiments	0	10	10	10	0	

2. Thermal Sensitivity of ES

There are a number of methods for the determination of the thermal sensitivity of ES. Let us consider those methods which are most commonly used.

Determination of flash point

There are two wide-spread variations of methods for the determination of flash point. In the first variation a bath, usually filled with fusible metal or with high boiling oil is heated to 100°C. When this temperature is reached a test tube with the specimen of the tested ES (usually 0.5 g; for ES which produce detonation, 0.1 g) is immersed and the bath is further heated at a rate of 20°C per minute. The temperature of the bath at which flash occurs is noted as well as the nature of decomposition. The nature of decomposition varies for different ES from the spontaneous flash with a weak, frequently hissing sound to the detonation-like explosion. Sometimes instead of a flash a more or less violent decomposition of ES takes place, not accompanied, however, by flame; sometimes the decomposition proceeds calmy. Heating is usually carried up to 360°C and the absence of flash is put on the record.

In the second variation the bath is maintained at a constan temperature and the ES sample is introduced into a preliminarily inserted, preheated test tube.

The delay of flash, i.e., the time τ between the moment of the introduction of ES and the moment of flash is recorded. It is worthwhile also to determine the minimum temperature of flash, i.e., the temperature, below which the decomposition proceeds without a flash. This temperature depends not only on the properties of the substance, but also on the conditions of the experiment: the amount of ES, the shape of the bottom of test tube, the thermal conductivity its material, the composition of the gas, the filling of the test tube, etc.

The relationship between the delay of flash and the temperature is expressed by curves, similar to the curve in Fig. 5.17, constructed for mercury fulminate. It is interesting to note that in log τ and $\frac{1}{T}$ coordinates the relationship between the delay of the flash and the temperature turns out to be linear, for many ES.

It was shown above (Chapter II, page 85 and 109), that such a dependence may lead to autocatalytic and chain reactions, completed by a thermal appearance of the explosion.

Table 5.17 gives the values of flash points for different ES, determined by the more commonly used first method.

Table 5.17. Flash Point of Different ES

ES	Temperature of flash, °C	ES	Temperature of flash, °C
Black powder	310-315	Dinitrobenzene	Does not produce flash
Sodium mine powder	305-315	Trinitrochlorobenzene	395-397
Pyroxylin	195-200	Trinitrotoluene	295-300
Collodion	204-205	Trinitroanisole	290-296
Smokeless powder	180-200	Hexanitrodiphenylamine	248-252
Nitroglycerine	200-205	Tetryl	190-194
PETN	205-215	Chlorate explosive (cheddite)	258-265
Guhr dynamite	195-200		
Blasting gelatin	202-208	Amatol 80/20	300
Gelatin dynamite	180-190	Lead azide	325-340
Hexogene	215-230	Mercury fulminate	170-180
Picric acid	300-310	Lead styphnate	270-280
Trinitrocresol	270-276		
Trinitrobenzene	Does not produce flash		

Table 5.18 gives the values of the flash points obtained by a somewhat different method. A sample of ES (0.02 g) in a copper primer case is placed in a bath with Wood's metal and a determination is made of the temperature at which a flash or a violent decomposition took place after 5 sec. Due to smaller samples and the large thermal conductivity of the walls of the case, as compared with

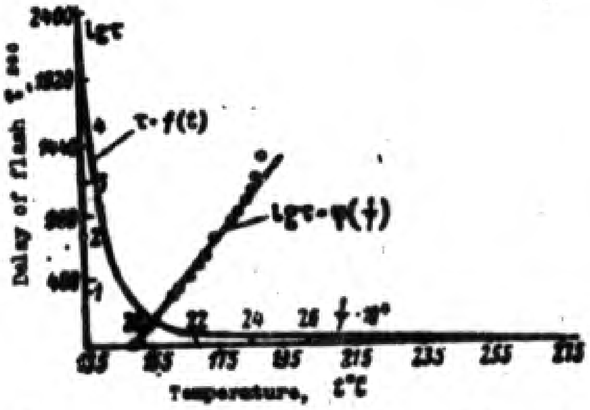

Fig. 5.17. Delay of flash of mercury fulminate as a function of temperature.

glass, the values of flash points, obtained by this method, are significantly higher than those given in Table 5.17. A comparison of the data of Tables 5.17 and 5.18 with Table 2.1 shows that the flash of condensed ES occurs, in general, at lower temperatures than of gas mixtures.

Table 5.18. Flash Point of Different ES

ES	Flash point, °C	ES	Flash point, °C
Glycolnitrate	257	Trinitrotoluene	475
Diethyleneglycoldinitrate	237	Picric acid	322
Nitroglycerine	222	Ammonium picrate	318
Erythritoltetranitrate	225	Tetryl	257
PETN	225	Hexyl	325
Dipentaerythrite hexanitrate	255	Mercury fulminate	210
Mannitol hexanitrate	205	Silver fulminate	170
Nitrocellulose (13.3% N)	230	Lead azide crystaline	345
Ethylenedinitramine	190	Diazodinitrophenol	180
Nitroguanidine	275	Lead styphnate	265
Hexogene	260	Lead dinitrosoresorcinate	265
Octogene	335	Tetrazene	154
Trinitrobenzene	550	Hexamethylenetriperoxidediamine	<149

Behavior of ES when dropped into a heated iron bath

The bottom of an iron bath is heated with a strong burner to red heat and in the center of it a little sample of ES (0.1-0.2 g) is dropped (taking the necessary precautions). The sample is gradually increased to 5 g. The behavior of ES under this test (intensity of burning, occurrence or absence of explosion) characterizes the degree of danger of ES during sudden contact with metal heated to a high temperature. Such contact can occur in case of fire during the manufacture, transport or storage of ES.

The behavior of ES with respect to a safety fuse (determination of the inflammability of ES)

A sample of ES weighing 0.1-1.0 g is placed in a test tube, into which one introduces a piece of safety fuse in such a way, that it just touched the surface of tested substance. Taking protective measures against fragments in the case of explosion, the cord is lit from above and one observes the behavior of ES during the action of the beam of fire from the cord. Depending on the properties of ES under these conditions it can detonate (primary ES), explosion or flash (black powder, pyroxylin), burning (tetryl, dynamite) or not to ignite at all (nitro compound, ammonites).

In another variation of this test the cord is placed at some distance away from the surface of ES and by successive trials one determines at what maximum distance the ignition still occurs.

Test on the campfire

A cubic box (10 cm on the sides) made from sheet iron, 1 mm thick, with tightly fitting cover is filled with the tested ES. After making a strong fire from dry wood, the box with ES is lowered onto it from a shelter. Note is made of the nature of the decomposition of ES and the extent of deformation of the box. The purpose of this test is to reproduce the behavior of ES in a metal enclosure under conditions of fire.

3. Sensitivity of ES to Detonation

Sensitivity to primer cap

This sensitivity is characterized by the minimum charge in the primer cap, which produces a complete explosion of ES. Tests are conducted to determine the action of ES by one of the methods accepted for this purpose, for instance in Trauzl bomb, on a lead cylinder, according to Hess, or on a brisance meter (see Chapter IX, page 677). At first one uses a primer cap with such an amount of charge, which is known insufficient to produce a full explosion of the tested ES. Consequently, one obtains a lower value for the expansion of the bomb or compression of cylinder during determination of brisance. One gradually increases as the charge in the following experiments approaching a limit, after which any further increase of primer charge will not result in a noticeable increase of the action of explosive. This is a limit which is expressed by the number of primer caps or the quantity of mercury fulminate, which comprises the charge of the primer cap (or equivalent to this charge), and thus characterizes the sensitivity of ES to a given form of the initial impulse. As an example it is possible to cite the results of the study of chloratite No. 3 (which is a mixture of potassium chlorate, wood meal (3%) and 0, 2, 5 and 10% kerosene. The values of compression which were obtained on the brisance meter with different size primer caps, are given in Table 5.19.

From the data of Table 5.19 it is clear that the sensitivity of chloratite increases with increase of kerosene content to 5%. Further increase of kerosene content to 10% lowers the sensitivity and ES does not explode even with the use of No. 8 primer caps.

Table 5.19. Results of the Test of Chloratite No. 3 for Sensitivity to Primer Caps

Kerosene content %	Compression of copper cylinders on brisance meter, in mm				
	Primer cap*				Picric acid powder + + primer cap No. 8
	No. 5	No. 6	No. 7	No. 8	
0	–	–	–	–	0.1 0.3
2	0.3 0.2	2.4 0.2	2.8 3.0 } 2.9	2.9 2.8 } 2.9	2.9 2.9 } 2.9
5	0.3 0.4	4.2 4.2 } 4.2	4.8 4.4 } 4.6	4.4 4.3 } 4.4	4.4 4.4 } 4.4
10	–	–	–	0.7 0.2	4.7 4.6 } 4.7

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*Charges of primer caps are equivalent to: No. 8-2 g of mercury fulminate, No. 7-1.5 g of mercury fulminate, No. 6-1.0 g of mercury fulminate and No. 5-0.8 g of mercury fulminate.

A practical criterion of the absence of the ability to explode

The determination of the sensitivity of ES to primer charge is intimately related in essence and in methodology to the problem of establishing the absence of the ability to explode for different substances. Practically, this question is very significant, especially in the establishment of conditions for the technical treatment and the storage of newly introduced materials. The degree of explosiveness limits the intensity of permissible influences on a given material in the course of processing and also determines the necessary precautionary measures. Moreover, in certain cases, for instance in selection of the composition of fertilizer mixtures, which include nitrates, one of the essential requirements is the absence of ability to explode.

The most intense of all practically encountered impulses is the action of the charge of explosive ES. Therefore, the practical solution of this question regarding the explosiveness of substance is reduced to determination of its behavior during the action of an explosion of the primer cap or of a large charge of ES. If the presence of the tested substance does not increase the action of explosion, then such a substance is considered nonexplosive.

It is a more complex problem if one observes an increase of the effectiveness of explosion on addition of the tested material, since this still does not constitute the fact that the tested substance is unconditionally explosive. Really, let us assume that this substance is not capable of exploding, but it is capable of exploding under the action of high temperatures of the products of explosion of the primer charge and the shock wave produced as for example ammonium sulfate. The presence of such a substance can lead to a certain increase of the action of explosion. This increase will be even more pronounced, if one were to take a nonexplosive mixture of ammonium sulfate with an explosive substance, for instance ammonium nitrate. However, in both cases an important criterion of the explosive process will be absent — the ability of this process to propagate spontaneously without limit. This is easily verified by using the same initiator but to increase the quantities of tested substance. Starting at some limiting value the increase of the general effect of the explosion will cease to be observed. Consequently, the propagation of the explosion throughout the whole mass of the substance, subjected to the action of initiator, will not occur. Practically this means that on the industrial scales the strength of the effect will not exceed the order of magnitude of the force of an explosion of the primer used.

A serious complication of such tests is the fact that the ability to explode, may be absent with small dimensions of the primer and charge of the tested substance, but it may appear with an increase of both. Due to this the limiting conditions of explosiveness obtained during tests should not be evaluated as absolute characteristics of substance.

The test proceedings is determined to a significant extent by the nature of the primer. If the test of a substance for explosiveness uses primer caps, then one normally uses the Trauzl test (see below page 677), in which a strong shell in the shape of the walls of a lead bomb and sand packing aid the explosion. If under such a test the investigated substance produces an expansion which is not larger than that due to primer cap itself or more exactly than a primer cap in combination with a known nonexplosive substance, then the tested substance is also considered not to be explosive.

As an example it is possible to cite a mixture of ammonium nitrate with potassium chloride. In 95:5 ratio such a mixture produces in a Trauzl bomb a significant stretching; 165 cm^3; when the ratio is 85:15 the expansion is 135 cm^3. At the same time a mixture of potassium nitrate and ammonium chloride, having the same elementary composition, but by themselves not able to explode under these conditions, produced an expansion of only 4-5 cm^3.

Tests in a Trauzl bomb with a primer cap cannot be considered as final. The absence of a noticeable additional expansion of the bomb may be caused not by the fact that the tested substance is incapable of exploding, and by the fact that it is tested in a charge, the diameter of which is significantly less than the critical diameter.

As follows from the Khariton's principle (see Chapter IV, § 12, Point 2), with increase of the dimensions of ES charge it can appear to be able to produce a stable detonation. Therefore, experiments in lead bomb are usually augmented with tests of large charges, using, at the same time, a more powerful initial impulse than the primer cap, and a strong shell. The biggest dimensions of the tested charge are determined by the practical problems of test. Sometimes it is necessary to test the ability of different substances to explode in the form of very large charges (boxes, drums, barrels of factory packaging, piles, etc).

During tests, for instance, of technical calcium nitrate, containing 13.2% of water and mineral oil, the following method was used for the determination of the relationship between the explosive properties and the content of oil and water. The substance was placed in steel tubes, 10 cm in diameter, closed from both ends, and primed by means of an explosion of charge of pressed picric acid, weighing 100 g. During the experiment with calcium nitrate, containing only moisture (13.2%), the tube was torn and unfolded only in the upper part, and the lower part remained absolutely intact (Fig. 5.18a). The explosion did not spread through calcium nitrate.

When the damp saltpeter contained 4% of oil the decomposition spread over a somewhat larger section, as shown in Fig. 5.18b, but part of calcium nitrate did not explode and the lower end of the tube remained intact.

In the third experiment the test was made on dry calcium nitrate containing up to 9% of oil. The whole tube (see Fig. 5.18c) was torn into a large number of pieces with ripped edges, which indicates the presence of explosion. Under these conditions the mixture of calcium nitrate and oil should be considered as capable of exploding.

Further experiments showed that the explosive tendency of dry calcium nitrate occurs only if the oil content exceeds 5%.

The quantitative evaluation of the explosiveness of those substances, which are capable of exploding, under various conditions encountered in their use is also of great practical significance. Such evaluation is done by determination of the critical and limiting diameters (see page 283), tests for completeness of detonation of the elongated charge and transmission of detonation under different conditions (see page 527).

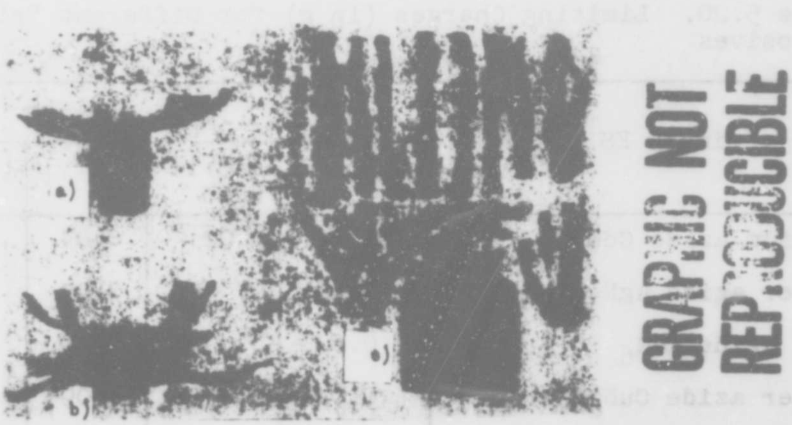

Fig. 5.18. Iron tubes after exploding in them calcium nitrate. a) with 13.2% moisture content; b) with 13.2% moisture and 4% oil content; c) dry calcium nitrate with 9% oil content.

4. Effectiveness of Initiating Impulse

<u>Determination of the initiating ability of primary explosives</u>

This determination is generally conducted by establishing a limiting charge of tested substance with respect to some single secondary ES. This method consists in the following.

The primer cap is filled with a definite density charge of secondary ES, for instance trotyl, tetryl, picric acid etc. The tested initiating substance is pressed over this charge. The operation of such a cap is determined by one of the methods accepted for this purpose (see below). Increase or decrease of the amount of primary ES during successive trials establishes its limiting (minimum) charge with respect to a given secondary ES. The values of limiting charges for certain primary ES with respect to trotyl, tetryl, picric acid and trinitroanisole are given (according to Wöhler) in Table 5.20.

Table 5.20. Limiting Charges (in g) for Different Primary Explosives

Primary ES	Secondary ES			
	Tetryl	Picric acid	Trotyl	Trinitroanisole
Cadmium azide CdN_6	0.01	0.02	0.04	0.1
Silver azide AgN_3	0.02	0.035	0.07	0.26
Lead azide PbN_6	0.025	0.025	0.09	0.28
Copper azide CuN_6	0.025	0.045	0.095	0.375
Mercury azide HgN_6	0.045	0.075	0.145	0.55
Thallium azide TlN_3	0.07	0.115	0.335	—
Cadmium fulminate $Cd(ONC)_2$	0.008	0.05	0.11	0.26
Silver fulminate $AgONC$	0.02	0.05	0.095	0.23
Copper fulminate $CuONC$	0.025	0.08	0.15	0.32
Mercury fulminate $Hg(ONC)_2$	0.29	0.30	0.36	0.37
Thallium fulminate $TlONC$	0.36	0.43	—	—

The values given in Table 5.20 for the limiting charges can not, however, be considered as absolute constants of the corresponding primary ES. Since the magnitude of limiting charge is determined mainly by the length of the section along which burning of primary ES is accelerated to detonation, then it depends on the form of the primary charge. In essence it is more correct to speak of the limiting (minimum) height of the charge of primary ES, sufficient for transition from burning to detonation, and not the limiting weight of the charge.

Test of the initiating action of primer caps

Different test methods of primer caps may be classed into two groups according to the initiating action: direct and indirect methods. In the case of indirect methods the measure of the initiating action usually constitutes a mechanical action of the explosion of the cap.

Indirect methods include the following.

Lead bomb test. A primer cap with fuze cord are introduced into a cylindrical lead bomb, 100 mm in height and 100 mm in diameter, with a cylindrical channel, 7 mm in diameter and 55 mm in depth. The expansion, produced by the explosion, characterizes the action of the primer cap. Results of experiments with primer caps containing 2 g charges of different ES are given in Table 5.21.

Table 5.21. Expansion of Primer Caps Containing Different Primary ES in a Lead Bomb

ES	Expansion cm^3	Limiting charge according to trotyl, g
Mercury fulminate	26.0	0.36
Lead azide	33.0	0.09
Silver azide	22.6	0.07
Diazobenzene nitrate	43.1	>0.5

From Table 5.21 it is clear that there is no correspondence between the initiating action and the expansion in the bomb. The expansion is determined basically by the heat of explosion of ES, and not by the rate of burning during igniting and brisance. These latter, however, determine the initiating effect.

Tests on lead plates (Fig. 5.19). The test is conducted by means of detonation of a primer cap, fixed vertically on 4-5 mm thick lead plate. The size of the produced dent or hole characterize the action of the primer cap. Along with this index of the initiating action (in the case of primers with metallic shell) consideration is given to the thickness of cracks, formed on the surface of the plate by shell fragments (Fig. 5.20). Sometimes, the loss of weight of the plate is also determined. This test is the most wide-spread and it justified itself sufficiently in use for flow method quality control of definite type primers and in checking their state upon warehouse storage.

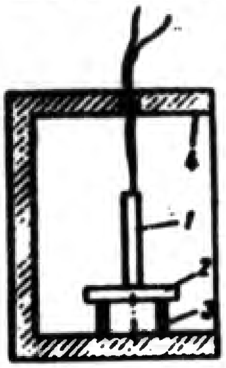

Fig. 5.19. Diagram of the test of primer caps on a lead plate. 1) electric detonator; 2) lead plate; 3) section of steel pipe; 4) protective housing.

Nail test. The primer cap is attached to a nail. During explosion the nail is bent (Fig. 5.21). The angle of flexure of nail serves as the characteristic of the action of the primer cap. This test is simple to perform, but in view of the heterogeneity of nails it produces large variations in parallel tests.

Sand test. The primer cap is detonated in a special steel bomb, filled with sand of definite grain size. The amount of sand pulverized by explosion is determined after the experiment by screening. This amount is characteristic of the action of the primer cap.

The basic weakness of all indirect methods of testing primer caps is the fact that the initiating action is judged from the mechanical effects: piercing of the plate, flexure of the nail, pulverizing of the sand etc. At the same time it is impossible to consider that initiating action is simply determined by these effects. Moreover, in some cases this is known not to be so. For instance, during tests of primer caps in a metal case with an indented bottom, the breakthrough action on the lead plate is much greater than in the case of a flat bottom. The initiating action, determined by direct method is not increased.

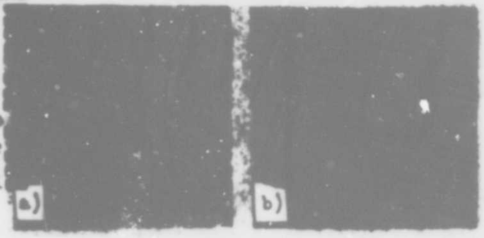

Fig. 5.20. The form of a plate after the experiment. a) normal action of primer cap; b) incomplete explosion.

For this reason indirect methods can be considered applicable only to the quality control of primers of the same construction, but not for the comparison of different types of primers charged with different types of ES. For the latter purpose one should use one of the many direct methods.

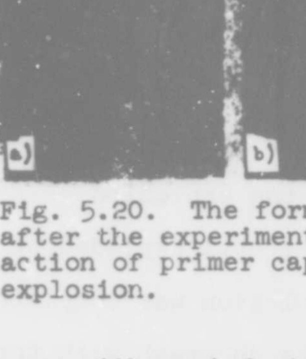

Fig. 5.21. Nail tests of primer caps. a) nail with primer cap before explosion; b) nails after explosion of different primers.

The _direct_ method determines directly the initiating action of the tested primers with respect to phlegmatized standard ES. The maximum content of deterrent, at which the primer still produces a complete explosion, serves as the measure of the initiating action. Variations of this method differ with respect to the selection of phlegmatized ES, deterrent and the method of establishment of the completeness of the explosion.

The direct method author Aesop (1899) used picric acid, phlegmatized with cotton-seed oil. He exploded the charges of phlegmatized picric acid on lead cylinders and he judged the completeness of explosion from the magnitude of the obtained compression. In a subsequent work he applied trotyl crystal, phlegmatized with paraffin oil (2-9%). The 2 g charge was pressed into a copper case. The case with charge and cap was mounted on a lead plate. The loss in weight of the plate after the explosion indicated, whether trotyl exploded or not and whether explosion was complete. Plotting the results on graph with the content of deterrent and loss in weight of plate as the coordinates it is possible to establish easily the maximum content of paraffin oil, at which one still obtains a complete explosion of phlegmatized trotyl (Fig. 5.22).

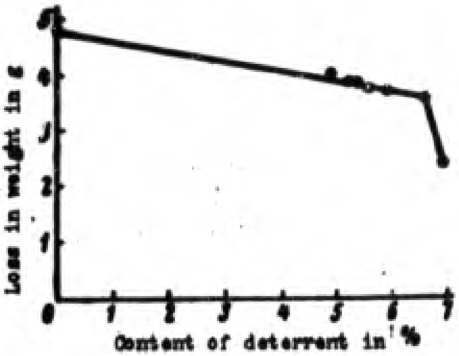

Fig. 5.22. Loss in weight of a lead plate upon explosion of phlegmatized trotyl as a function of the content of deterrent.

Subsequently talcum was suggested as a deterrent. The advantage of talc is in that trotyl phlegmatized by it does not change its sensitivity during storage, in contrast to that which was observed during phlegmatization by paraffin oil or paraffin. Also, the introduction of paraffin oil has a limit (9%) above which the oil is squeezed out during pressing, while for talc, being a solid, this limitation does not exist. Finally, since trotyl is moderated by talc to a smaller degree, it is necessary to use it in large quantities, so that any possible errors in dosage are less significant in this case than in the case of paraffin oil. A certain draw-back of the use of talc is the difficulty of distributing it uniformly in trotyl as compared with liquid deterrent.

To establish the completeness of explosion Haid exploded pressed cartridges of phlegmatized trotyl on lead plates. The dimensions and the nature of dents served as the characteristic measure of the explosion. This method was checked in our Artillery Academy and gave positive results. Therefore, it is a shame that it has not been used till now in practice. The need for a reliable method is especially great for correct evaluation of the influence of a number of realized or proposed innovations on the effectiveness of primer caps (primers in paper shells, with dent in the lower part and without it, lowering of the requirements for moisture proofing at primers etc).

CHAPTER VI

SHOCK WAVES

§ 1. Basic Properties of Shock Waves and the Mechanism of Their Occurrence

As was already noted above, the shock wave is a region of compression with an abrupt change of pressure, density and temperature on the leading front, propagating in a medium with supersonic speed.

Shock waves appear during explosions and can spread in any media: air, water, earth, concrete, metal, etc. The most important practice and, therefore, the most studies is the case of shock waves in air. Air shock waves are sometimes also called blast wave. Subsequently, we will consider primarily the air medium. Shock waves in water and earth will be briefly considered at the end of the chapter.

During an explosion of a spherical charge of ES in an unbound uniform medium the region of the shock wave (region of compression) constitutes a spherical layer, the center of which coincides with the center of the explosion, but the radius of which continuously increases with time.

Due to shock waves the destructive action of the explosion can be transmitted through the medium for significant distances, exceeding considerably those which can be directly affected by the expanding products of explosion. With the development of military technology the role of shock waves as a striking factor continuously increases. During the explosion of large ammunition (large caliber aerial bombs), explosions of large shells, and also during nuclear explosions it is the shock wave which produces destruction at significant distances and is the basic striking factor. In the beginning of our century shock waves were nothing more than a curious physical phenomenon, yet now shock waves have a most important practical use.

Fig. 6.1 shows a typical curve for the change of pressure with time p(t) at a certain space point during the passage of a shock wave, caused by an explosion. Such a curve maybe recorded experimentally, for instance with the aid of a piezoelectric transducer and an oscillograph.

At the time of arrival of the shock wave at a given space point the pressure is abruptly increased from value p_0 (initial pressure of the medium) to value p_1 at the front of shock wave (point A in Fig. 6.1). The abruptness of this change may be seen from the fact that in very strong shock waves the transition for p_0 to p_1 is accomplished over a distance of several lengths of the mean free path of molecules. After a shock front the pressure drops rapidly and upon the expiration of time t_+ from the moment of the arrival of the shock wave it becomes lower than the initial pressure p_0, at point B, the compression phase is replaced by the rarefaction phase. In the front of the shock wave the substance at a given space point will start to move with speed w in the direction of the propagation of the wave. The occurrence of a unique

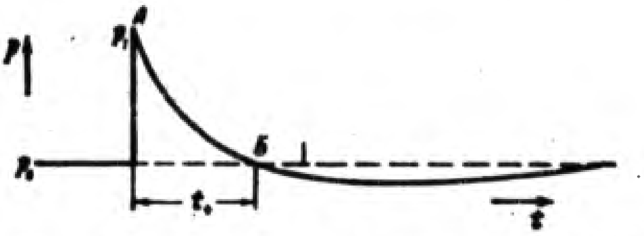

Fig. 6.1. Change of pressure with time during passage of an explosion shock wave.

"wind" flow is characteristic of shock waves. For behind the front of the wave the speed of flow is lowered. The nature of change of $w(t)$ after the front, just as the nature of change of density $\rho(t)$, is similar to the nature of change of $p(t)$.

The leading front of a shock wave spreads with speed D, which, as we saw, exceeds speed of flow of substance $(D > w)$, and also speed of wound in the medium $(D > c_0)$. Differing from c_0 the speeds D and w are variable. They become lower as the propagation and weakening of the shock wave takes place. In the limit, at very large distances from the origin of explosion, the shock wave turns into an acoustic wave, the speed of propagation of which approaches the speed of sound, and the speed of flow will be reduced to zero.

In the beginning of this paragraph we defined a shock wave as a region of compression. In reality, we see that a shock wave consists of a compression phase, followed directly by a rarefaction phase. Nonetheless the above formulation may be preserved. The fact is that the destructive action of a shock wave is determined by the compression phase. The rarefaction phase is in this respect immaterial, and its destructive action is usually not considered, with the exception of certain specific effects. The basic nature of the compression phase, determining the destructive power is the excess pressure on the front of a shock wave

$$\Delta p = p_1 - p_0.$$

Subsequently, we shall indeed see that under certain conditions the destructive power is determined by the magnitude of a specific impulse * of the compression phase:

$$I = \int_0^{\tau_+} \Delta p(t)\, dt.$$

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*Specific impulse is an impulse of pressure forces, per unit area. The normal technological dimensions of specific impulse are $kg \cdot sec/m^2$.

nonetheless the magnitude of excess pressure at the front, Δp, is the most important parameter of shock wave*.

Near the center of the explosion of pressure at the front of shock wave is sufficiently great and is measured in tens and even hundreds of atmospheres. However, as the propagation of the wave proceeds and the distance from the center of explosion increases, the pressure drops rapidly. One should not think that in practice one is interested only in strong shock waves with pressure on tens and hundreds of atmosphere. In reality weak shock waves are also very important with pressures of only several tenths of an atmosphere. The fact is that if an air shock wave is caused by an explosion of great capacity, for instance the explosion of an atomic bomb, then at excess pressure of front of 0.2-0.3 kg/cm^2 it is still able to cause significant destruction to a majority of city buildings made of brick and wood. At excess pressures of 0.6-0.7 kg/cm^2 it will destroy structures with steel frames and light concrete buildings. Excess pressure of 1.0 kg/cm^2 leads to complete destruction of all structures. Approximately the same pressure, in the case of shock waves of powerful explosion, having large duration, evokes lethal injury to living organisms**.

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*The sign Δ is used for the designation of small differences. As applied in the theory of shock waves it has no relationship to the designation Δp: the difference Δp is usually either not too different in order of magnitude from p_0 or it may be many times greater than it.

**The figures (0.2-1.0 kg/cm^2) seem small because the pressures refer to a small area (1 cm^2). Let us remember, therefore, that pressure 0.2 kg/cm^2) corresponds to 2 t/m^2.

Near the center of the explosion, where the pressures are measured in atmospheres and tens of atmospheres, the destruction is very intense, but it embraces a small area. Conversely, moderate pressures, which are still sufficient to produce serious destructions, embrace very large areas. Let us take for 100% the area of circle, inside of which the pressure of a shock wave during a ground explosion is not less then 0.2 kg/cm^2. Then the area of the action of shock waves with various pressures will be as follows:

from 0.2 to 2 kg/cm^2	92%
from 2 to 20 kg/cm^2	6.7%
20 kg/cm^2 and above	1.3%

We see that in the large part of the destruction region relatively weak waves are operative.

The occurrence and propagation of a shock wave in air may be depicted by a simple model, shown in Fig. 6.2, which we already used in deriving fundamental equations of the hydrodynamic theory of detonation.

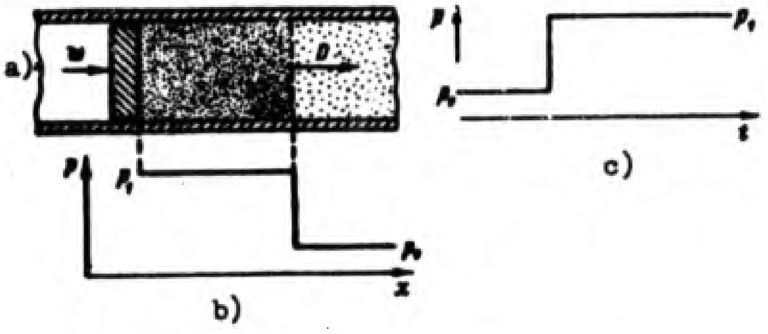

Fig. 6.2. Formations of shock wave by moving piston. a) diagram of a pipe with piston, b) distribution of pressure along the length of the pipe at a certain moment, c) change of pressure with time at a certain point inside the pipe.

With constant speed w, a piston is inserted into a pipe filled with air. The air, adjacent to the piston will begin to move with this same speed. In the air packing will occur with increase of pressure at the leading front, which will spread with speed D > w. Thus, the motion of the piston will lead to the formation of shock wave, although, somewhat different from the typical shock wave produced by an explosion. The change of the pressure of a shock wave, produced by the piston, moving with constant speed in the pipe with time, under the conditions, when not a spherical, divergent, wave is formed but a plane one-dimensional shock wave, depicted in Fig. 6.2c. On the leading edge of the shock wave the pressure (and also the density, temperature, and speed of flow) changes sharply, but then it preserves a constant value (in a typical explosion shock-wave it rapidly decreases after the front).

In order for a piston to produce a shock wave, its speed must be sufficiently great, but not necessarily supersonic. If the speed of the piston is of the order of the speed of sound (in air), then the excess pressure at the front of the shock wave will be of the order of several atmospheres; at the speed of piston of 50 m/sec the excess pressure at the front of shock wave will be of the order of 0.25 kg/cm^2. It was already noted that such pressure is sufficient for the destruction of many city buildings. Even at the speed of the piston of only 10 m/sec, $\Delta p_1 \approx 0.05$ kg/cm^2; the shock wave with such pressure may cause light destruction, in particular breakage of glass. Let us stress that here we speak of the shock wave, which occurs during motion of a nonstreamlined piston. If a well streamlined body moves in air (for instance an aircraft or a missile), then any significant pressure jump will appear only at speeds of flight, close to the speed of sound.

Let us now consider various conditions of motion of the piston. Let us assume that its motion is accelerated periodically. Then the recording of p(t) in any cross section of the pipe will have the form, shown in Fig. 6.3 at the top, and will consist of a number of steps, each of which corresponds to the intermittent increase of the speed of the piston. The distribution of pressures

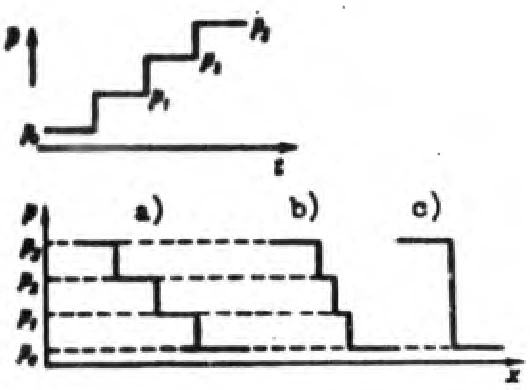

Fig. 6.3. Formation of shock waves by piston, which is accelerated periodically. Above – change of pressure with time in a certain section of pipe. At the bottom – a, b and c are distribution curves of pressures along the length of the pipe in three consecutive time intervals.

along the length of the pipe at a certain moment is shown in the lower part of Fig. 6.3, on the graph a. The following circumstance is very important: dynamically compressed gas is heated, and the speed of propagation of perturbations in it is increased. Therefore, even in the case, when $p_2 - p_1 = p_1 - p_0$, the speed of wave D_2, moving along the compressed, heated gas, will be larger than D_1 – the speed of wave, moving along the undisturbed gas. In turn speed D_3 of the wave along the doubly compressed gas will be still larger than D_2. Inasmuch as $D_3 > D_2 > D_1$, the latter jumps will catch up with the former. The distribution of pressures along the axis of the pipe in consecutive moments is shown in graph b of Fig. 6.3. Finally, all jumps will unite into one powerful shock wave, shown in the lower part of Fig. 6.3 on graph c.

Let us assume now that the perturbation in the beginning has smooth front (Fig. 6.4a), let us note that such a fron maybe obtained during smooth acceleration of the motion of piston. The speed of propagation of perturbations at the apex of the wave will be larger than at the base. As a result the wave front will be rapidly transformed, becoming steeper (see Fig. 6.4, a, b and c). Thus, a compression wave of finite amplitude, causing a significant heating of the medium during passage, can spread stably only in the form of a shock wave with pressure jump at the front (a smooth front is unstable and is transformed into a jump).

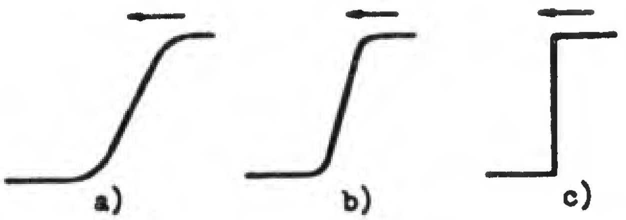

Fig. 6.4. Transformation of a smooth front of compression wave into a shock wave.

Let us return again to the piston, moving evenly, and let us assume that this piston began to slow down or even stopped. During the time of motion the piston performed work and it conveyed to the air some definite amount of energy. At the expense of this energy the propagation of shock wave will continue even after the ceasing of the motion of piston. Now the shock wave itself, with a flow of substance behind its front, will play the role of the piston with respect to the undisturbed air. The profile of shock wave [curve p(t)] after stoppage of the piston should change significantly. Inasmuch as the air will continue to move, then in the region, adjacent to the piston a relative rarefaction will occur.

Thus, as a result of the stoppage of the piston curve p(t) on Fig. 6.2 will become similar to curve p(t) on Fig. 6.1 for a typical shock wave of an explosion with the characteristic fast drop of pressure after the front. For such a typical shock wave it is necessary to note the following important circumstance: its front spreads with speed D, its trailing side (that part, where pressure becomes close to p_0) spreads with a speed close to speed of sound in the initial state c_0. Inasmuch as $D > c_0$, the leading edge of the shock wave will spread faster than its trailing edge. As the wave propagates it is continuously stretched in time.

The above considered diagram for the formation of a shock wave by a moving piston maybe applied also to the mechanism of the formation of shock wave during an explosion. Gaseous products of the explosion compressed to high pressures play the role of a unique piston, interacting on the medium in all directions and causing the formation of shock wave. The products of explosion constitute a three-dimensional piston, moving from the center of the explosion to the periphery. In the initial moments they have the greatest speed of scattering. As the expansion proceeds the speed of scattering drops to zero, after which gases are shifted to a certain extent in the opposite direction. Thus, during the explosion we deal with a similar phenomenon influence of the piston which suddenly starts to move with great speed and then it is slowed down and stopped. Therefore curve p(t) for the shock wave of explosion near the center of the explosion has the form shown in Fig. 6.1, and it is characterized by the fast lowering of the pressure behind the front.

For to solve certain problems it is important to know, to what distance (from the center of spherical charge) the piston action of explosion products continues i.e., at what distance is the shock wave detached from the propping explosion products and begins its "independent" existence with that reserve of energy, which was transmitted to it in the process of the expansion of the explosion products. It is difficult to determine exactly the distance of the breakaway of the shock wave from the products of explosion, more so, because this breaking away occurs not suddenly but gradually. It is usually accepted that during the explosion of a spherical charge in the air the shock wave is detached from the products of explosion at a distance of the order of 8-15 charge radii. On the average it is possible to take this distance to be equal 12 charge radii. The pressure on the front of the shock wave at this distance from explosion center is still sufficiently great; about 10-20 kg/cm^2;

the speed of propagation of wave here is D ≈ 1000-1400 m/sec and the speed of flow after the front w ≈ 800-1200 m/sec.

As the propagation of shock wave proceeds, the pressure at the front, just as the speeds D and w, drops rapidly for several reasons.

If the wave is spherical (divergent), then in the course of propagation the energy is distributed over a greater and greater surface. As a result the energy, per unit surface of shock wave, should decrease even in the absence of losses. Lowering of the energy per unit surface leads to a decrease of pressure.

Furthermore, as was already noted above, in the course of propagation of the shock wave it is stretched in time, which even at a constant impulse should lead to lowering of the pressure.

Furthermore, during propagation of a strong shock wave the temperature of the air, through which it passed, even after the passage of the wave is somewhat higher than the initial temperature ("thermal trace" of shock wave); part of the energy is expended for this heating, which also results in a pressure drop.

All of the listed factors act in one direction and rapidly (especially in the case of strong spherical waves) lower the pressure on front of shock wave in the course of its propagation.

The above considered basic properties of shock waves allow us to formulate the most important differences in the nature of shock waves and acoustic waves.

1. Changes of pressure, density and temperature of medium, thorugh which an acoustic wave passes, are insignificantly small as compared with the initial pressure, density and temperature the acoustic wave, then, constitutes a stable form of the propagation of very weak perturbations.

On front of a shock wave a finite and discountinuous change of pressure, density and temperature occurs. The shock wave constitutes a form of propagation of strong perturbations, when changes of the parameters of the medium during compression cannot be considered insignificant as compared with the initial conditions.

2. The speed of the propagation of sound in a given uniform medium under a given set of initial conditions is constant.

The speed of propagation of the shock wave front is not constant but dependent on the intensity of the pressure jump. As a rule, the shock wave propagates with speed, higher than the speed of sound.

3.During the propagation of an acoustic wave the oscillating motion of particles of the medium occurs; a finite shift of the medium is practically absent.

During the propagation of shock wave a flow of substance occurs behind it. This flow is stronger, the stronger the shock wave. In the compression phase the flow moves in the direction of the propagation of the shock wave, while in the rarefaction phase a weaker (with smaller speed) motion in opposite direction takes place. This results in a finite shift of the substance of the medium in the direction of propagation of the wave.

In the course of propagation of a shock wave it weakens, its excess pressure decreases to insignificantly small value, the speed of propagation decreases and in the limit it approaches the speed of sound. The speed of flow decreases to zero. At a sufficiently large distance from the source of explosion the shock wave becomes a usual acoustic wave.

From the above-stated it follows that their exists no sharp boundary between a weak shock wave and strong acoustic waves. There exist perturbation of such intensities, which may equally be called weak shock waves or strong acoustic waves. The boundary between them is arbitrary and it depends on the circumstances, the nature of the problem on hand, the necessary accuracy, etc.

In the theory of shock waves one sometimes distinguishes strong and weak waves. Strong shock waves (strong explosions) are called waves with such a large pressure on the front that in comparison to it the initial pressure is minute and it may be neglected. It is obvious that the boundary between the strong and the weak shock waves is still less definite that the boundary between the shock waves and the acoustic waves.

§ 2. Some Quantitative Relations Between Basic Wave Parameters

The basic parameters of the shock wave, to be defined include the following five magnitudes: pressure on front p_1, density ρ_1, and temperature T_1 of the substance in the front of the wave, speed of propagation of front D, and speed of flow of substance after it w. As was shown in Chapter IV in examining the hydrodynamic theory of detonation, equation of conservation of matter, momentum, and energy during compression; and also the equation of the state of the substance compressible by the wave give four relationships between the five indicated parameters. Given one of them, one can determine all the others, by establishing their simple connection with the given value, and also with the parameters, characterizing the initial state of the medium.

We shall select, as the given value, practically the most important magnitude Δp, equal to $p_1 - p_0$, and will establish the connection

$$D = f_1(\Delta p);\quad w = f_2(\Delta p);\quad \rho = f_3(\Delta p)\ \text{and}\ T = f_4(\Delta p).$$

From the law of conservation of momentum (4.44) follows

$$\Delta p = \rho_0 D w. \qquad (6.1)$$

From the equation of conservation of matter (4.43) we obtain

$$w = D\left(1 - \frac{\rho_0}{\rho_1}\right). \qquad (6.2)$$

Consequently.

$$\Delta p = \rho_0 D^2\left(1 - \frac{\rho_0}{\rho_1}\right). \qquad (6.3)$$

Substituting in formula (6.3) value ρ_0/ρ_1 from the formula of dynamic adiabatic curve for an ideal gas (4.53)

$$\frac{\rho_0}{\rho_1} = \frac{(k-1)p_1 + (k+1)p_0}{(k+1)p_1 + (k-1)p_0},$$

by making simple conversions and replacing $k\frac{p_0}{\rho_0}$ with c_0^2, we obtain

$$\Delta p = \frac{2\rho_0}{k+1}(D^2 - c_0^2), \qquad (6.4)$$

whence

$$D = \sqrt{\frac{(k+1)\Delta p}{2\rho_0} + c_0^2}. \qquad (6.5)$$

Further, from (6.1) we obtain

$$w = \frac{\Delta p}{\rho_0 D} = \frac{\Delta p}{\sqrt{\frac{(k+1)\Delta p\rho_0}{2} + c_0^2\rho_0^2}}. \qquad (6.6)$$

From equation (4.53) it directly follows that

$$\frac{\rho_1}{\rho_0} = \frac{(k+1)(\Delta p + p_0) + (k-1)p_0}{(k-1)(\Delta p + p_0) + (k+1)p_0}. \qquad (6.7)$$

For the ratio of temperatures, we obtain

$$\frac{T_1}{T_0}=\frac{p_1}{p_0}\frac{v_1}{v_0}. \qquad (6.8)$$

Considering that

$$\frac{v_1}{v_0}=\frac{\rho_0}{\rho_1}$$

and substituting in (6.8) the value ρ_1/ρ_0 from formula (6.7) we obtain

$$\frac{T_1}{T_0}=\left(\frac{\Delta p+p_0}{p_0}\right)\left[\frac{(k-1)(\Delta p+p_0)+(k+1)p_0}{(k+1)(\Delta p+p_0)+(k-1)p_0}\right]. \qquad (6.9)$$

Introducing a new magnitude – local speed of sound c_1 in the front of the shock wave (i.e., the speed with which small perturbations in the air are propagated, which having the same state as on the front of the shock wave), at the same time we introduce a new relationship:

$$c_1=\sqrt{k\frac{p_1}{\rho_1}}=\sqrt{k\frac{\Delta p+p_0}{\rho_1}}. \qquad (6.10)$$

Replacing in (6.10) the value ρ_1 from equation (6.7), we obtain

$$c_1=\sqrt{\frac{k(\Delta p+p_0)}{\rho_0}\,\frac{(k-1)(\Delta p+p_0)+(k+1)p_0}{(k+1)(\Delta p+p_0)+(k-1)p_0}}. \qquad (6.11)$$

In Table 6.1 are the values of D, w, c_1, $\frac{\rho_1}{\rho_0}$, $\frac{T_1}{T_0}$ in function Δp, calculated by formulas (6.3-6.11) for the values of p_0, ρ_0, T_0, c_0, corresponding to the international standard atmosphere. Calculation is carried out with variable value of k, i.e., taking into account the variations of heat capacities. The values of k are estimated by magnitude of internal energy of gas at corresponding temperatures and pressures. The data below the line, i.e., the data pertaining to pressures from 30 to 100 kg/cm^2, are not very reliable. If calculation of parameters is necessary when $\Delta p > 100$ kg/cm², then one must consider not only the variation of heat capacity of air, but also its partial dissociation and ionization occurring at high temperatures.

The data in Table 6.1 are plotted on the graphs of Fig. 6.5 and 6.6.

Table 6.1. Parameters of Shock Wave Front In Air
$p_0 = 1.033$ kg/cm²; $\rho_0 = 1.25 \cdot 10^{-3}$ g/cm³; $T_0 = 288$°K; $c_0 = 340$ m/sec

Δp in kg/cm²	D in m/sec	u in m/sec	c_1 in m/sec	ρ_1/ρ_0	T_1/T_0
0,05	347	11,5	342	1,034	1,014
0,10	354	22,6	345	1,068	1,028
0,15	361	33,3	347	1,101	1,040
0,20	367	43,6	349	1,134	1,053
0,25	374	53,5	351	1,167	1,064
0,30	379	63,4	353	1,200	1,076
0,40	393	81,4	357	1,262	1,100
0,50	405	98,7	360	1,324	1,121
0,70	428	131	367	1,442	1,164
1,00	461	174	377	1,606	1,226
1,40	501	223	388	1,811	1,301
2,0	560	288	406	2,083	1,409
3,0	636	375	428	2,47	1,58
4,0	707	453	450	2,785	1,75
5,0	778	514	469	3,06	1,91
6,0	831	578	489	3,295	2,07
7,0	887	632	508	3,48	2,23
8,0	938	682	524	3,67	2,38
9,0	986	729	544	3,82	2,54
10,0	1034	771	556	3,95	2,705
12,0	1122	856	585	4,21	3,00
15,0	1242	966	626	4,51	3,44
20,0	1418	1128	686	4,895	4,16
30,0	1715	1400	784	5,465	5,50
40	1986	1630	864	5,80	6,75
50	2192	1825	936	6,20	7,97
70	2586	2182	1050	6,74	10,21
100	3040	2630	1180	7,42	13,20

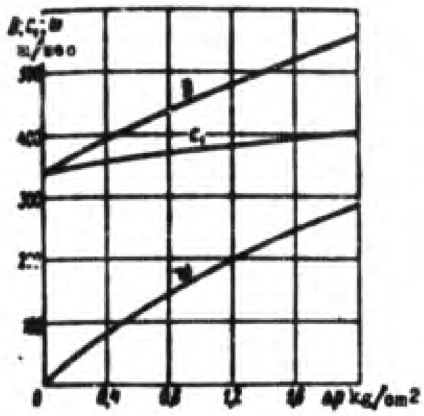

Fig. 6.5. Parameters of shock waves in air with values of Δp up to 2 kg/cm^2.

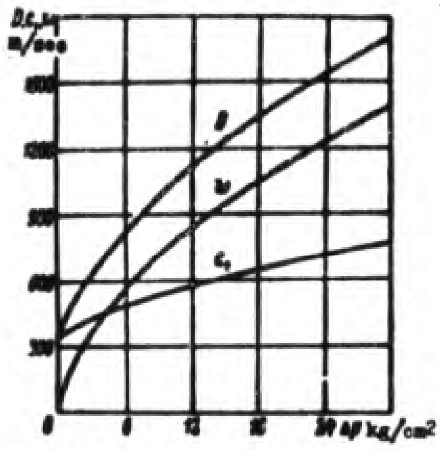

Fig. 6.6. Parameters of shock waves in air with values of Δp from 2 to 30 kg/cm^2.

§ 3. Basic Factors of Destroying Action of Shock Waves and Elements of Law of Similitude During Explosions

For a full appraisal of the destroying action of an explosion it is necessary to know the character of the charge and properties of the structure on which this charge acts. The most complete characteristic of a charge is given by p(t) – excess pressure in function of time.

In certain cases it is possible to essentially simplify the task and consider that the destroying action of a shock wave is determined either by excess pressure on its front

$$\Delta p = p_1 - p_0.$$

or by the magnitude of specific impulse of the phase of compression:

$$I_+ = \int_0^{t_+} \Delta p(t)\,dt.$$

The shock wave of an extremely powerful explosion, for instance the explosion of an atomic bomb, explosion of a large ammunition dump, etc., is rather intense at large distances and has a long duration. Time of action t_+ by the phase of compression of such a shock wave usually exceeds the period T of natural oscillations of elements of the structures*.

If $t_+ >> T$, the destroying action is basically determined by the magnitude of excess pressure. In this case the time of existence of excess pressure in the wave (t_+) does not directly enter the characteristic of destroying action. This time is taken with a surplus: if pressure is sufficiently great the structure is deformed and will be destroyed after such time (on the order of 1/3 to 1/4 T), after which the pressure in the shock wave will not fall very significantly. If pressure is insufficient and deformation of the structure caused by it from the very beginning does not lead to its destruction, the structure will not be destroyed in the subsequent moments when pressure starts to drop.

This case, when destruction is determined by excess pressure (shock wave of very powerful explosions), is often conditionally called static action of the shock wave.

If the shock wave is caused by an explosion of low power (explosion of ordinary single ammunition, artillery shells, high-explosive aerial bombs of low and medium caliber, etc.), then at those distances where the shock wave is still sufficiently intense the duration of the phase of compression t_+ is less than the period of natural oscillations T of typical structures or their parts. In case $t_+ << T$, pressure after the front will fall after so short an interval of time that the structure practically will not be able to be moved from the place. However, under action of the impulse of

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* For typical structures, buildings and their parts, T is several hundredths or several tenths of a second.

the phase of compression the structure will obtain a certain momentum and will be subsequently destroyed if this momentum is enough to cause some limiting deformation; destruction in this case will already occur after the phase of compression passes.

Thus, if $t_+ << T$, the destroying action is determined by the impulse of the phase of compression imparted to the structure. This case is often conditionally called the impulsive action of the shock wave.

If t_+ in order of magnitude does not differ too much from T, then the character of the action of the shock wave will be, in a known measure, intermediate between the purely impulsive and static action. Destroying action in this case is impossible to estimate by the magnitude of excess pressure or by the magnitude of specific impulse: it will be determined by a certain head part of the impulse. In such cases, for appraisal of destroying action it is necessary to know the entire courve of $p(t)$.

For appraisal of destroying action of the shock wave of an explosion, the law of similitude during explosion has a fundamental value; its elements will be presented below.

The law of similitude allows us to estimate and compare the magnitudes of excess pressures and impulses of shock waves caused by explosions of charges of various weight and even absolutely different nature. This possibility is exceptionally important. Almost all empirical formulas applied for appraisal of the destructive action of shock waves are essentially partial applications of the law similitude.

On this law in particular is based the possibility of simulating superpowerful explosions.

The most simply formulated are the deductions of the law of similitude for excess pressure. The magnitude of excess pressure of the shock wave of an explosion may be estimated, if one knows distance R from center of the charge and is given the characteristics of the explosion itself. In order to completely characterize the explosion, it is necessary, as we will see further, to know its full energy and initial air pressure. In certain cases, a sufficient characteristic is the weight of the charge or even its linear dimensions.

Before we turn to the basic deductions of the law of similitude, it is necessary to indicate some essential conditions of its successful application.

Let us imagine that in a homogeneous medium an explosive charge of spherical form is exploded. Then the shock wave will diverge equally to all sides and its consecutive positions will be a row of spheres with a common center coinciding with the center of the charge. The field of pressures will be centrally symmetrical, and for appraisal of excess pressure it is sufficient to give the distance to the center of the explosion, not indicating direction: all directions in this case are equivalent. The possibility of use of the law of similitude in such a case of spherical symmetry is essentially facilitated.

It is significantly more complicated to solve the problem if the form of the charge differs from spherical (for instance, cubic, cylindrical, and others). The surface of the shock wave of the explosion of such charges, especially near the center of explosion, is not a sphere, and the magnitude of pressure at identical distances will be different for various directions.

The fact is that in the initial moment of products of the explosion move in directions perpendicular to the surfaces of the charge. If, for instance, a charge is detonated in the form of a cube, the products in the beginning will move in directions perpendicular to its sides, and pressure in these directions at identical distances from the center will be greater than in the directions of the diagonals. Appearing with such an explosion, the shock wave at identical distances from the center will have a higher speed of propagation and correspondingly greater pressure in the direction of the sides of the charge than in the direction of its diagonals. Only at some distance from the center of explosion does the surface of the shock wave become spherical, and practically the same as from the spherical charge. This distance is quite great: for charges whose form does not differ too much from a sphere (cube, cylinder with height equal to diameter, etc.), the distinction of parameters of the shock wave in various directions is still noticeable at a distance of several tens of radii of the charge; for charges whose form sharply differs from a sphere (elongated cylinder, disk, etc.), the distinction is still noticeable at a distance of 100-150 radii (smallest dimensions) of the charge.

If charges are not spherical, then for not too large distances with the use of the law of similitude the following additional conditions must be observed:

1. Comparison should be made for charges of similar form.
2. The effects should be compared for similar directions (i.e., for instance, in the case of a cylinder either in the direction of the axis, or in a direction, perpendicular to it, or in the direction of the corners. By comparing two charges, it is impossible to determine for one the effect in the direction of the lateral sides, and for the other – in the direction of the axis of the cylinder).

Subsequently, the absence of special indications about the direction and assignment of only the magnitude of distance will signify that the simplest case is being considered — the spherical shock wave, formed by explosion of a spherical charge, or a distance so great that a nonspherical charge at such distance already gives a spherical wave.

The simplest case of the law of similitude during explosions is the so-called <u>geometric law of similitude</u>, according to which, distance R, at which is observed some definite value of Δp_1^*, in proportion to radius r of the charge*

$$R_{(\Delta p_1^*)} = ar. \qquad (6.12)$$

If, for instance, a charge with radius r_1 gives pressure Δp_1^* at distance R_1, then a charge with radius r_2 will give the same pressure Δp_1^* at distance R_2, whereby

$$\frac{R_1}{R_2} = \frac{r_1}{r_2}. \qquad (6.13)$$

If Δp_1 is not given and we must determine what Δp_1 will be observed at distance R, then according to the geometric law of similitude

$$\Delta p_1 = f\left(\frac{r}{R}\right). \qquad (6.14)$$

The form of function f should be established from experience.

The very simple geometric law of similitude has, however, extremely limited application. In the above-stated form it may be applied only to charges made from the same explosive and having identical density. If we take charges of the same explosive, but of different density, relationships (6.12)-(6.14) cannot be applied.

In a more general case — different densities — instead of radius of charge, as a basic parameter we take magnitude $\sqrt[3]{C}$, where C is the weight of the charge. The law of similitude in this form

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*Here and further we will write Δp_1 in order to emphasize that we are concerned with excess pressure on the wave front.

may be called the generalized geometric law of similitude. According to this law

$$R_{(\Delta p_1)} = a_1 \sqrt[3]{C}. \tag{6.15}$$

If, for instance; a charge with weight C_1 creates pressure Δp_1^* at distance R_1, then another charge with weight C_2 will create the same pressure at distance R_2; whereupon

$$\frac{R_1}{R_2} = \sqrt[3]{\frac{C_1}{C_2}}. \tag{6.16}$$

If the more general problem of the dependence of Δp_1 on distance, is solved then according to the generalized gemometric law of similitude

$$\Delta p_1 = f\left(\frac{\sqrt[3]{C}}{R}\right). \tag{6.17}$$

The form of function f is determined from experience. In the future this form will be given.

Magnitude

$$\bar{R} = \frac{R}{\sqrt[3]{C}} \tag{6.18}$$

is called given distance; in accordance with (6.17) magnitude Δp_1 is a single-value function of given distance. In calculations of given distance, just as in the calculations with respect to equation (6.17), a technical system of units is applied and R (and also r) is substituted in meters and C in kilograms.

If one compares expressions, (6.14) and (6.17), it is obvious that magnitude $\sqrt[3]{C}$ as if replaces the radius of the charge. We shall give the numerical connection between magnitudes r and $\sqrt[3]{C}$ when density of charge $\rho = 1.0$ g/cm^3. It is obvious that

$$r = \sqrt[3]{\frac{3}{4\pi\delta}}\sqrt[3]{C}.$$

where δ is the specific gravity of the explosive.

With the use of the technical system of units of density, $\rho = 1.0\ g/cm^3$ will correspond to specific gravity $\delta = 10^3\ kg/m^3$. Whereby

$$r = \frac{1}{16}\sqrt[3]{C}, \text{ or } \sqrt[3]{C} = 16r.$$

Consequently, if $\rho = 1.0\ g/cm^3$, then magnitude $\sqrt[3]{C}$, utilized as the "given" radius of the charge, is approximately 16 times more that the usual radius of the charge.

Earlier it was established that breaking away of the shock wave from the products occurs at a distance of 10-15 radii of the charge. It follows from this that given distance $\bar{R} = 1$ is somewhat greater than the distance of breakaway of the shock wave. When $\bar{R} < 1$, on the environment act the shock wave and products of the explosion; when $\bar{R} \geq 1$ the object is subjected to the influence of only the shock wave.

The generalized geometric law of similitude which contains parameter $\sqrt[3]{C}/R$ instead of parameter r/R, can be applied more widely and, in particular, for charges of different density. However, the possibilities of this law also are limited. Experience shows that if one takes charges of different explosives having equal weight, but different energy, then the charge with high energy will render a stronger action at an identical distance. This is absolutely natural: the energy of the shock wave, which is combined with its destructive action, should depend not on the weight of the charge C, but on the energy of the explosion $E = CQ_v$, where Q_v is the specific heat of the explosion. Thus, in the most general case, a basic parameter of the law of similitude during explosions should not be parameter $\sqrt[3]{C}/R$, but parameter $\sqrt[3]{E}/R$.

This version, developed by L. I. Sedov and M. A. Sadovskiy, carries that name of the energy law of similitude during explosion. The energy law may be applied not only for a comparison of charges of different explosives, but also for comparison of explosions of essentially different nature, for instance explosions of an explosive substance on the one hand, and explosions which are electrical, atomic, volcanic, etc. For successful comparison of these explosions it is sufficient to know the energy given off in each case. Here, indeed, it is necessary to make a certain reservation. The fact is that essentially parameter $\sqrt[3]{E}/R$ should not include total energy of the explosion E, but energy of the shock wave, which composes a certain share of the total energy of the explosion $E_{ex} = \eta E$, where $\eta < 1$. If explosions of different nature are compared, then magnitude η can differ somewhat, but it is necessary to emphasize that this difference is small. For an explosive it is possible to disregard the variation of η, and with an accuracy sufficient for practical purposes, substitute total energy of explosion in criterion $\sqrt[3]{E}/R$.

It is possible to use criterion $\sqrt[3]{C}/R$, which includes weight of the charge C in such a way that it essentially becomes an energy criterion. For that it is necessary, as the weight of the charge, to substitute its energy equivalent, i.e., the weight of such a charge of a standard explosive (usually trotyl), the energy of which is equal to the energy of explosion of the given charge.

In the first approximation it is possible to consider that

$$C_{\text{экв}} = C\frac{Q}{Q_{\text{ТНТ}}}.$$

[ЭКВ = equ = equal; ТНТ = TNT]

where C is the weight of the selected charge; C_{equ} is its trotyl equivalent: Q is its specific heat of explosion: Q_{TNT} is specific heat of explosion of trotyl.

As the last magnitude, we usually select the rounded-off value of $Q_{TNT} = 1000$ kcal/kg. This value pertains to trotyl of great density (pressed or cast). Trotyl of low (filled) density has a lower heat of explosion. Let us note further that ammonite No. 6 has a heat of explosion close to 1000 kcal/kg; therefore, the trotyl equivalent of the charge is practically equal to its equivalent with respect to ammonite No. 6.

For an example we shall take 1 kg of nitroglycerine; the heat of its explosion is ~1500 kcal, i.e., one and a half times higher than for trotyl. Let us assume that we must determine Δp_1 at a certain distance R with the help of formula (6.17), where the form of function f is established for trotyl. Applying this function for nitroglycerine, as C it is necessary to substitute not 1 kg, but the equivalent weight with respect to trotyl, i.e., $C_{equ} = 1.5$ kg.

With the use of the trotyl equivalent, formula (6.17) in essence the energy formula, although the weight of the charge is directly included in it. It allows us to compare not only explosions of charges of different explosives, but also explosions of different nature. It is possible to apply formula (6.17), with numerical coefficients fixed for trotyl to explosions of atomic, volcanic nature, etc.; only as C it is necessary to substitute the weight of the charge of trotyl, equivalent in energy to the given explosion.

Essentially, with the use of equivalent trotyl charges in calculations, the weight of trotyl plays the role of a unique energy unit:

1 kg	trinitrotoluene	.... 10^3 kcal
1 t	"	.... 10^6 "
1 kt (10^3t)	"	.... 10^9 "
1 mt (10^6t)	"	.... 10^{12} "

Subsequently, in Chapter IX, we will see that it would be more correct to substitute not the weight equivalent with respect to energy, but the weight equivalent with respect to full work. However, this remark has more of a fundamental value, rather than practical.

Let us give data on the form of function f in formula (6.17). As a result of extensive research conducted by M. A. Sadovskiy, the form of this function is exactly established for trotyl and, consequently, for any form of explosion with the use of the trotyl equivalent. From the foreign sources on this question one should note the work by Stoner and Blickney. For pressure of the air shock wave from the explosion of a charge of spherical (or close to it) form, spreading in free air without interaction with the earth's surface, we have*

$$\Delta p_1 = \frac{0.84}{\bar{R}} + \frac{2.7}{\bar{R}^2} + \frac{7.0}{\bar{R}^3}. \qquad (6.19)$$

If the explosion occurs on the surface of the earth and the shock wave spreads along the surface, pressure will be somewhat greater:

$$\Delta p_1 = \frac{1.06}{\bar{R}} + \frac{4.3}{\bar{R}^2} + \frac{14}{\bar{R}^3}. \qquad (6.20)$$

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*Let us recall once again that in the calculation of given radius $\bar{R}$ by formula (6.18), distance should be substituted in meters, and weight of charges in kilograms.

Formulas (6.19) and (6.20) are derived for the range of variation of $\overline{R}$ from 1 to 10-15. When $\overline{R} < 1$, these formulas can give an essential error. In Table 6.2 are given values of Δp_1 calculated formulas (6.19) and (6.20). The first column of values of $\Delta p_{1\ sur}$ – propagation on surface from ground explosion: the second column Δp_{air} – propagation in free air.

Table 6.2 Excess Pressures Δp_1 of Air Shock Wave Depending Upon Given Distances $\overline{R}$

$\overline{R}=\frac{R}{\sqrt[3]{C}}$	$\Delta p_{1\,sur}$ kg/cm^2	$\Delta p_{1\,air}$ kg/cm^2	$\overline{R}=\frac{R}{\sqrt[3]{C}}$	$\Delta p_{1\,sur}$ kg/cm^2	$\Delta p_{1\,air}$ kg/cm^2
15	0,094	0.07	3,0	1,36	0,85
12	0,126	—	2,75	1,63	—
10	0,163	0,118	2,50	2,00	1,21
9	0,19	—	2,0	3,35	1,90
8	0,227	0,161	1,8	4,21	2,50
7	0,281	—	1,6	5,75	3,29
6	0,36	0,247	1,4	7,94	4,52
5	0,406	0,332	1,3	9,73	5,43
4,5	0,602	—	1,2	12,00	6,60
4,0	0,743	0,486	1,1	15,00	8,20
3,5	0,981	—	1,0	19,4	10,1

The data in Table 6.2 are drawn on the graph in Fig. 6.7. The upper curve corresponds to the case of propagation of a shock wave on the surface, and the lower, to propagation in free air. By using the graph and knowing $\overline{R}$, one can determine Δp_1 or solve an inverse problem.

Let us consider an example. Let us assume that a charge of hexogene weighing 2.5 t explodes on the surface of the earth; it is required to determine the pressure on the front of the wave at distance R = 50 m. We shall take the heat of the explosion of hexogene to be equal to 1300 kcal/kg; then a trotyl charge equivalent in energy is equal to

$$C_{экв} = C_{гекс} \cdot \frac{Q_{гекс}}{Q_{тнт}} =$$

$$= 2500 \frac{1300}{1000} = 3250 \text{ kg}$$

[гекс = hex = hexogene]

Given distance

$$\bar{R} = \frac{50}{\sqrt[3]{3250}} = 3.4.$$

We find for a surface charge when $\bar{R} = 3.4$

$$\Delta p_1 = 1.05 \text{ kg/cm}^2.$$

We shall solve the inverse problem: on the surface of the earth explodes a charge of ammonite having a total weight of 10 t, or 10^4 kg; heat of the explosion of ammonite is equal to the heat of the explosion of trotyl. We must determine at what distance from the center of the explosion will the excess pressure be equal to 0.25 kg/cm². We find that pressure $\Delta p_1 = 0.25$ kg/cm² corresponds to $\bar{R} = 7.5$; hence the sought distance.

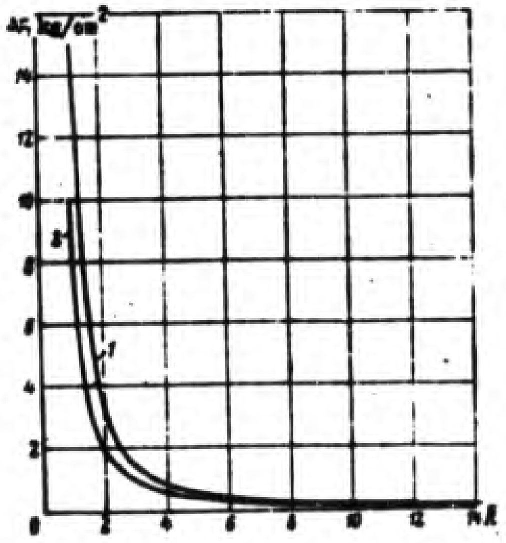

Fig. 6.7. Excess pressure Δp_1 on the front of the spherical shock wave of an explosion in the function of given distance $\bar{R}$. 1) explosion of surface of earth; 2) explosion in air.

$$R = \bar{R}\sqrt[3]{C} = 7.5\sqrt[3]{10^4} \approx 160 \text{ м}.$$

Finally, if we know Δp_1 and R, we can determine C_{equ}. Later, in the chapter on the workings of an explosion we will see that this is the basis of one of the methods of evaluating the efficiency of explosives.

Let us recall that if a charge with trotyl equivalent C_1 has a known pressure Δp_1 at distance R_1, then one can easily determine at what distance R_2 will charge with trotyl equivalent C_2 give the same value of Δp_1; this may be done with help of equation (6.16) without the use of formulas with specific coefficients, tables, or graphs.

Let us stop very briefly on the question of magnitude of the impulse of the shock wave of an explosion.

The use of the law of similitude and experimental research conducted for the first time by M. A. Sadovskiy, indicate that at distances $\bar{R} > 0.5$ the magnitude of specific impulse of the shock wave of an explosion may be estimated by the following simple formula:

$$I = A\frac{C^{2/3}}{R} = A\frac{C^{1/3}}{\bar{R}} \quad \text{kg sec/m}^2. \qquad (6.21)$$

Some data on the value of coefficient A will be given subsequently.

Near the charge ($\bar{R} < 0.25$) the magnitude of specific impulse is usually estimated by a formula of another form:

$$I = B\frac{C}{R^2}. \qquad (6.22)$$

Finally, for the time of action of the compression phase t_+, M. A. Sadovskiy offered the formula

$$t_+ \approx \sqrt[6]{C}\sqrt{\bar{R}} \cdot 10^{-3} \text{ sec}. \qquad (6.23)$$

The above-mentioned formulas for pressure pertained to the case of propagation of a spherical shock wave. In the propagation of shock waves through pipes and channels, the walls prevent divergence of the shock wave and it is converted into a flat wave; the laws of change of pressure with distance thereby essentially change. If we disregard friction of the shock wave against the walls, the impulse of the shock wave practically remains constant, pressure is lowered with propagation, but significantly weaker than in the case of a spherical shock wave. The pressure of strong flat waves is lowered with distance according to the law

$$\Delta p_1 \sim \frac{1}{R}.$$

and weak waves

$$\Delta p_1 \sim \frac{1}{\sqrt{R}}.$$

§ 4. Change of Pressure in Shock Wave with Time

For a complete estimate of the destroying action of a shock wave it is necessary to know the change of pressure in the function of time.

Let us emphasize that knowledge of the curve p(t) allows us to determine excess pressure on the front Δp_1, the magnitude of specific impulse, and several other magnitudes. Therefore, in this course we do not give data on the methods and instruments determining only Δp_1 or only I, and are limited to a short account of the methods of recording p(t).

Fig. 6.8 gives a diagram of recording p(t) for a shock wave propagating in a homogeneous air medium; this recording has the normal "classical" form. Excess pressure on the front Δp_1 is determined directly by measurement of the maximum ordinate: the scale of pressures along the axis of ordinates is established from calibration experiments. Direct measurement of the abscissa determines t_+ — the time of action of the compression phase; is the system of time marks gives the scale for the axis of abscissas.

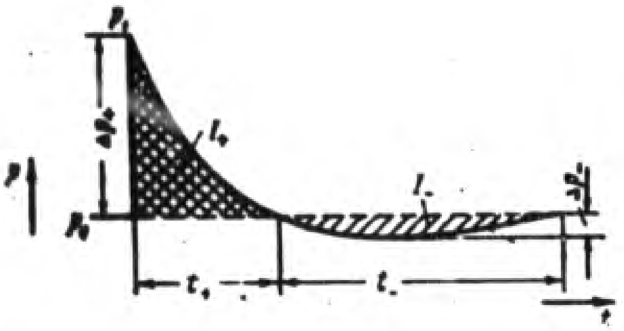

Fig. 6.8. Diagram of recording the change of excess pressure in the shock wave of an explosion in time.

Analogously, we can determine Δp_- – excess pressure in the rarefaction ($p < p_0$; therefore, magnitude $p - p_0$ is negative) and t_- is the time of action of the rarefaction phase.

Specific impulse of the compression phase I_+ is proportional to area S, shaded in Fig. 6.8 by double lines. If area S is determined (which is usually done graphically), then for calculation of impulse it is necessary to know the scales of the axes, i.e., the relations $\Delta p_1 = f(y)$ and $t_+ = \varphi(x)$. If pressure and time are linear functions of corresponding coordinates $\Delta p_1 = by$; $t_+ = ax$, then

$$I_+ = abS.$$

If pressure is measured in kg/cm^2 and time in seconds, the dimension of specific impulse will be in kg sec/cm^2; in practice, impulse is usually measured in kg sec/m^2.

Impulse of the rarefaction phase (single shading in Fig. 6.8) may be calculated analogously.

The instruments recording p(t) for the stock waves of an explosion are presented with high requirements with respect to time allotment. Their period of natural oscillations T should be significantly less than the time of action of the wave t_+.

If T is only somewhat less than t_+ (or even $T > t_+$), the recording will be greatly distorted; such a case is depicted in

Fig. 6.9a, where the solid line shows the true curve of p(t), and the dotted line – its recording by an instrument with relatively large T. The forward front of the wave is "filled up", and the value of Δp_1 is significantly less than its actual value; simply speaking, an instrument with low natural frequency cannot record "peak" pressure. The same instrument may be successfully used for recording p(t) of a longer wave (Fig. 6.9b). In this case the front is also "filled up", but the general form of the wave is much less distorted. The fixed value of Δp_1 practically does not differ front the true value. One should tentatively consider that the natural period of oscillations of the instrument T should be such, that during that time the pressure would not decrease by more than 2-5%.

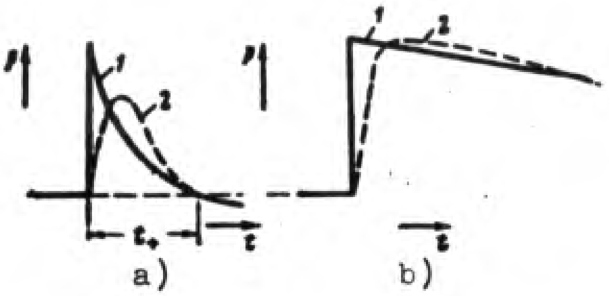

Fig. 6.9. Recordings of curve p(t) by instruments with insufficiently high natural frequency. a) wave of short duration; b) wave of significant duration; 1) true curve; 2) recording obtained by instrument.

We shall schematically describe the method of recording p(t) based on the use of the piezoelectric effect. If from the crystals of certain substances – piezoelectric crystals – we cut plates in a determined manner, then with the influence on them of forces guided in certain directions, there appear electrical charges on the edge of the plates proportional to the applied force.

If F is the applied force and Q the charge, then

$$Q = KF,$$

where K is the piezoelectric modulus and is constant for the given substance.

Appearance of the charge Q leads to the appearance of electrical voltage which is usually amplified by a special device and fed to a galvanometer or cathode oscillograph which throws out a beam.

Evolvement of the beam in time gives a recording of p(t). For an estimate of the change of pressure Δp according to deflection of the beam they preliminarily conduct calibration experiments. Calibration is done by various methods: static pressure with subsequent calculation of the so-called dynamic coefficient which is calculated for the given conditions; calibration is accomplished with devices simulating the dynamic action of a shock wave; in particular, in practice they widely apply calibration with shock waves having known values of Δp_1.

In addition, the following method of calibration is applied. Above we saw that excess pressure on the front Δp_1 and speed of propagation of the shock wave D are connected by dependence (6.4). If on a small base we precisely measure the speed of propagation of a shock wave (the base should be such that the speed of propagation on it would change minutely), then by applying formula (6.4) it is easy to find magnitude Δp_1, and then compare it with the indications of the piezomethod. Here, only the piezosensors should possess sufficiently high natural frequency f or, consequently, a short period of natural oscillations T ($f = 1/T$), so that during the time T, the pressure in the wave would not fall by more than 2-5%.

In spite of the fact that the principle of work of piezo-sensors is very simple, designing of reliable, full-value instruments was combined with the surmounting of significant technical difficulties. At present there exist fully reliable designs with high natural frequency exceeding 50-100 kilocycles. Such sensors allow us to record p(t) from an explosion of charges weighing 10-20 g and even 1 g (duration of phase of compression $\sim 10^{-4}$ sec).

As piezoelectric crystals, besides quartz, possessing high durability and high constancy piezoelecric properties, they use tourmaline; barium titanate is also a prospective material.

Under field conditions, with the explosion of comparatively big charges they usually apply the simplest methods of recording p(t). On the one hand, under field conditions it is not always possible to apply methods requiring comparatively complicated equipment; on the other hand, deeper shock waves with large t_+ can be successfully fixed with simple methods. As an example, let us point out strain gauges, whose principle of action consists in the fact that during the deformation of a steel diaphragm with a thin wire glued to it in a definite manner, the electrical resistance of the latter changes, which is fixed by an oscillograph. For very deep waves caused by superpowerful explosions, curve p(t) may be recorded with sufficient accuracy by simple mechanical instruments.

The dependence on time of change of pressure and other parameters — density, temperature, rate of flow behind the front of the shock wave — can be obtained not only experimentally, but also from theoretical calculations. Such calculations are very complicated and reducing them to a numerical result became possible only with the appearance of contemporary high-speed electronic computers.

Fig. 6.10 shows in dimensionless coordinates the change of pressure behind the front, calculated theoretically. On the x-axis is plotted time t in fractions of full time of action of compression phase t/t_+, along the y-axis is plotted the relation of current value of pressure to peak pressure of the wave. Each curve corresponds to a definite value of given distance and excess pressure on the front. From the graph it is clear that the more excess pressure there is on the front, the relatively faster it drops behind the front.

It should be borne in mind that in Fig. 6.10 the abscissa is figured not in absolute, but relative time. Let us take, for instance, two shock waves: one with pressure on the front $\Delta p_1 = 2.0$ kg/cm^2 (curve 3), having very long duration $t_+ = 0.1$ sec, and the other — with less pressure $\Delta p_1 = 0.17$ kg/cm^2 (curve 5), but with total time of action 0.01 sec. In identical relative time, lowering of pressure will be greater in the first wave. If one were to refer the drop of pressure to identical absolute time, the result would be reversed. Let us take, for instance, the time as 5 milliseconds. Then in the second case

$$\frac{t}{t_+}=\frac{5}{10}=0.5;$$

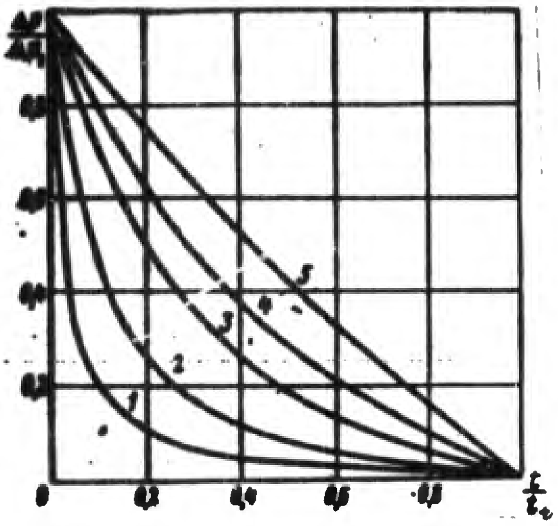

Fig. 6.10. Computed curves of changes of pressure behind the front of a shock wave. Each curve corresponds to a definite value of given distance $\bar{R}$ and excess pressure of the front Δp.

Number of curve	$\bar{R}$	Δp, kg/cm^2
1	0,70	[illegible]
2	1,30	[illegible]
3	[illegible]	[illegible]
4	[illegible]	[illegible]
5	7,9	0,17

from the graph it is clear that pressure will then fall by more than half. For the first wave

$$\frac{t}{t_+} = \frac{5}{100} = 0,05,$$

i.e., pressure will be lowered by approximately 15%.

With the help of the curves depicted in Fig. 6.10, it is possible beforehand to estimate the time during which the pressure falls by 2-5%, and thus determine whether or not the instrument with given natural period of oscillations for undistorted recording of p(t) of the given shock wave is suitable.

§ 5. Safe Distances for the Action of a Shock Wave

The problem of determination of safe distance for the action of a shock wave has a large practical value and may be solved by methods of the theory of similitude. The form of the calculating formula depends on the fact that in this case we are determining the destruction of the object of interest to us — maximum pressure or impulse of the wave (see p. 7). If the destroying action is determined by excess pressure on the front of the shock wave, distance R_{safe} is considered safe when Δp_1 does not exceed a certain value of Δp_1^* which is alreayd insufficient for destruction of a determined structure. Excess pressure Δp_1^* corresponds to the determined value of $\bar{R}^*$. In turn,

$$\bar{R}^* = \frac{R_{\text{без}}}{\sqrt[3]{C}}.$$

or

$$R_{\text{без}}=\bar{K}'\sqrt[3]{C}=K_1C^{1/3}. \quad (6.24)$$

[без = safe]

where the value of K_1 is determined by the properties of the destroyed object.

Analogously it is possible to show that if destruction is determined by the magnitude of impulse, then

$$R_{\text{без}}=K_2C^{2/3}. \quad (6.25)$$

In the "Single rules of safety while conducting explosive operations" the distances which are safe with respect to the action of the shock wave are recommended to be calculated by the formula

$$R_{\text{без}}=KC^{1/2}. \quad (6.26)$$

The exponent of C in formula (6.26) is the intermediate between exponents of formulas (6.24) and (6.25). This is more or less natural, if one considers the wide possibilities of change of the situation during explosions, and also the circumstance that in practice it is difficult to decide whether pressure or impulse determines the destroying action, especially when taking into account that often T is of the same order as t_+.

The values of coefficient K in formula (6.26) depend on the conditions of the explosion and character of the destruction. In Table 6.3 are presented some values of K recommended by the "Single rules of safety while conducting explosive operations".

On the basis of the data in the table we can make the conclusion that in an explosion of an exposed charge, the safe distance* to an inhabited locality is

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*Without calculation of scattering of fragments.

$$R_{\text{без}} > 10\sqrt{C}.$$

More detailed information concerning safe distances are given in the "Single rules of safety while conducting explosive operations".

Table 6.3. Value of Coefficient K in the Formula $R_{safe} = KC^{1/2}$ (C – in kg, R – in m)

Possible destruction	Value of coefficient K	
	Exposed charge	Charge, depressed into its height
Full destruction of glass, partial damage to frames, doors, disturbance of plastering and interior light partitions	5–8	2–4
Destruction of interior partition, frames, doors, barracks, barns, and so forth	2–4	1.1–1.9
Destruction of unstable stone and wooden buildings, upsetting of railroad cars, damage to electric power transmission lines	1.5–2.0	0.5–1.0

Let us emphasize that in the case of superpowerful explosions, for instance atomic, explosions of very large ammunition dumps, etc., when the destroying action is determined by excess pressure, calculation of safe distances by formula (6.26) gives knowingly overestimated results. In this case it is necessary to calculate by formula (6.24), where the values of K_1 also depend on the character of the possible destruction.

Table 6.4 gives tentative data on the values of Δp_1^* where there appears a determined form of destruction, and corresponding value of $\bar{R}^*$ for ground explosion.

Let us not that the data in Table 6.3 allow us to calculate the distances at which the definite form of destruction practically no longer occurs, and Table 6.4 gives the distances at which the definite form of destruction still appears. Therefore, the calculation of safe distances with the use of the data in Table 6.4 (for superpowerful explosions) should be done with the formula $R_{safe} > \overline{R}^* \sqrt[3]{C}$. Practically, magnitude $\overline{R}^* \sqrt[3]{C}$ should be increased by 1.5-2.0 times.

Table 6.4. Values of Excess Pressure of Front Δp_1^* and Corresponding Values of $\overline{R}^* = K_1$ in Formula (6.24) for Superpowerful Explosions on the Surface

Excess pressure Δp_1 kg/cm^2	Given distance $\overline{R}^*$	Form of destruction
0,1—0,2	15—10	Partial destruction of structures
0,2—0,3	9—7	Significant destruction of large city structures
0,6—0,7	4,5—4,0	Destruction of buildings with steel frames and light reinforced concrete structures
1,0	3,5	Full destruction of all buildings, including reinforced concrete earthquake-proof structures
1,5—2,0	2,8—2,5	Destruction and serious damage to reinforced concrete earthquake-proof structures
2,0—3,0	2,5—2,0	Displacement of steel girder bridges

§ 6. Safe Distance for Detonation

After consideration of the question of distances which are safe with respect to the destroying action of the shock wave, it would be appropriate to briefly mention the determination of distances which are safe with respect to detonation.

The phenomenon of a detonation consists in the fact that in the explosion of one charge, another one can explode at a certain distance. This phenomenon is also sometimes called detonation by effect (see Chapter V).

In practice, the distance for the transmission of a detonation is experimentally determined according to the diagram shown in Fig. 6.11. The result is usually judged by the state of the metallic, for instance brass, lining – the "witness." If a passive charge is detonated, the lining under it receives a dent. One should bear in

Fig. 6.11. Diagram of experimental determination of distance for the transmission of a detonation. A) active charge; П) passive charge; Д) lining — "witness."

mind that the phenomenon of transmission of a detonation, in any case with transmission through the air, carries a probability character, just as, for instance, the origination of an explosion from an impact. Therefore, each distance is usually subjected to several experiments and as the characteristic boundary we take the distance at which the probability of transmission of detonation is 50%. The phenomenon of transmission of a detonation is very complicated, especially if one were to consider that it practically can occur through various media (air, water, ground, metal, etc.). In this course we will be limited to the consideration of transmission of a detonation through air, where the distance of transmission is an order higher than in the other media. We will consider only the case of free distribution charges (see Fig. 6.11). Let us note that in canalize transmission, when, for instance, both charges are joined by a tube, the distances of transmission of detonation substantially increase.

In the transmission of a detonation through air, the passive charge is usually directly influenced by the products of explosion of the active charge: only in rare cases when the detonation is transmitted at a significant distance, only the shock wave acts, and the products of explosion cease to play a role. Further, if in an explosion there appear fragments (for instance, in the explosion of a charge in a shell), then the impact of even one fragment, independently of the action of the shock wave, can transmit the detonation to a significant distance.

From all this it is clear that inclusion of the section concerning transmission of detonation in the chapter on shock waves is conditional. At the same time it is necessary to note that in some cases there can be such conditions when transmission of a detonation through water, metal, etc. is knowingly accomplished by the shock wave.

The range of detonation depends on the characteristics of both active and passive charges. Different properties are important for active and passive charges. Decisive for active charge are its weight and specific energy, i.e., essentially the magnitude of the trotyl equivalent, and also the form of the charge and its location with respect to the passive charge. If, for instance, a cylindrical charge is used, then along its axis the range of transmission will be other than in lateral directions. Essential also is the value of the speed of detonation and density of the active charge. For a passive charge, the most important properties determining the range of detonation are sensitivity of the explosive depending on its chemical nature, density of the explosive size of crystals, and also the structure of the charge and its geometry. The higher the sensitivity of the explosive, the smaller the density and size of the crystals, and the greater the range (with an identical active charge) of the detonation. The type of casing has an essential value both for the active and passive charge.

For an estimate of distances which are safe with respect to detonation a formula of the same type is applied as in the calculation of distances which are safe with respect to the destroying action of a shock wave:

$$R_{\text{без.пер}}=K_{\text{пер}}C^{1/3}; \qquad (6.27)$$

[пер = det = detonation]

here C is the weight of the active charge in kilograms. Magnitude K_{det} is determined first of all by the sensitivity of the passive charge, and also by the intensity of the active charge.

Table 6.5 contains selective data on the value of coefficient K_{det} taken from the "Single rules of safety while conducting explosive operations."

Table 6.5. Value of Coefficient K_{det} in Formula (6.27) for Calculation of Distances Which are Safe with Respect to Detonation, for Exposed Charges

Active charge	Passive charge		
	Ammonite	40% dynamite	Trotyl
Ammonite	0,25	0,35	0,40
40% Dynamite	0,50	0,70	0,80
Trotyl	0,80	1,00	1,20

If substances are applied which are more powerful and sensitive than the explosives given in Table 6.5 (tetryl, PETN, hexogene), then the coefficient must be increased.

The question concerning detonation and calculating formulas undoubtedly needs further development. In this respect it is possible to indicate, for instance, that the data on coefficients given in the "Single rules of safety while conducting explosive operations," although "official," they are insufficiently founded and somewhat contradictory. Moreover, certain doubts are caused even by the very form of formula (6.27). Prospecting experiments conducted by Belyayev, Sadovskiy and Tamm show that if active charges of concentrated form (sphere, cube, cylinder with height equal to diameter) are observed with similarity both in form and in direction, and distance is computed from the center of the active charge, the range of detonation should be determined by the formula

$$R_{\text{без.дет}} = K_{\text{дет}} C^{1/3}. \qquad (6.28)$$

If as C, we substitute the weight of an equivalent trotyl charge, then for spherical active charges coefficient K_{det} will be determined only by the sensitivity of the passive charge. Above we already saw that the dependence of form of (6.28) is obtained from the law of similarity for pressure on the front. From this, the conclusion can be made that the range of detonation for a given passive charge is determined first of all by the magnitude of excess pressure on the front. Formula (6.28) was checked in laboratory conditions for comparatively small charges. There are indications that it is also valid for big charges.

Depending upon sensitivity of the passive explosive, its density and structure of the charge, the pressures on the wave front, which are sufficient for detonation, are measured in thousands, hundreds or even only in tens of atmospheres. Such pressures are knowingly insufficient, by means of compression of the most condensed explosive, to cause any significant heating up in it. Therefore, in a detonation, actuation of the reaction undoubtedly should be carried out by means of compression and heating up of the air found in the pores of the passive charge, or layers of air bordering on the charge, heating by heat transfer from the products, and also, possibly, by means of friction of particles. Stable conditions of detonation in the passive charge do not appear at once, but with some delay, which usually constitutes several microseconds. During this delay, the fast burning appearing in the passive charge is accelerated under the conditions of increased pressure and changes into a detonation.

It is interesting to note that under certain conditions detonation in the passive charge appears not on its surface, but at a certain depth, which also indicates the complicated character of the phenomenon.

§ 7. Interaction of Shock Waves with an Obstacle

Until recently, we considered propagation of a shock wave either in free air or along the surface. In practice very frequently the shock wave comes in contact with various kinds of obstacles. The character of its action then changes: the pressure and impulse transmitted by the obstacle are increased, as compared to the pressure and impulse of a freely propagating shock wave.

Fig. 6.12 shows graphs of distribution of pressure depending upon distance during the repercussion of a shock wave. Graph a corresponds to the moment when the wave approaches an obstacle. This obstacle may be a vertical wall during propagation of a shock wave along the surface of the earth or the surface of the earth itself, if the shock wave approaches from above. It is assumed that the obstacle has unlimited dimensions (in lateral directions) and is not destroyed.

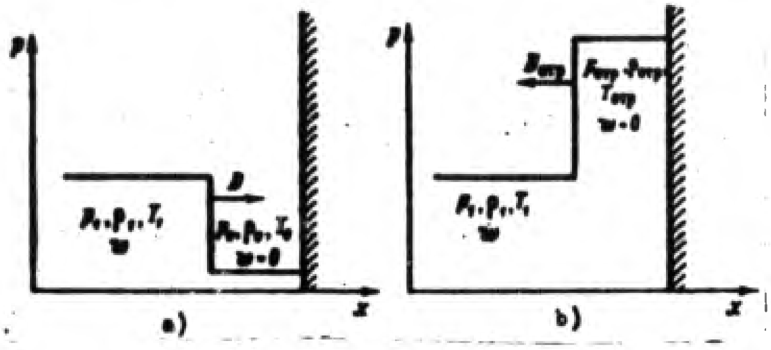

Fig. 6.12. Diagram of reflection of a shock wave from an obstacle. a) distribution of pressures in space at the moment preceding the approach of the front to the obstacle; b) the same, after reflection of the wave from the obstacle. [отр = ref = = reflection]

For simplification we assume that in approaching the wall the shock wave (it is usually called a traveling wave) has constant values after its front: pressure p_1, density ρ_1, temperature T_1, rate of flow w. At the moment when the shock wave encounters the wall, its front layer is braked and the rate of flow in this layer becomes equal to zero. Due to this braking there occurs an additional increase of pressure to value p_{ref}.

Let us remember that the pressure experienced by structures during a hurricane appears exclusively due to braking of the flow of air. During a hurricane, the speeds of flow reach several tens of meters per second. It is clear that upon braking the "flow" of a shock wave often having a speed of 100 meters per second, there can appear a very significant additional increase of pressure. In the following moment the next layer of the shock wave will encounter the braked layer and will be braked itself. Thus, braking will overlap one layer after the other, and on the traveling (incident) wave in a direction opposite to its motion (i.e., from the wall), will proceed a wave of additional compression which is usually called a reflected wave (Fig. 6.12b).

Applying the laws of conservation of matter, momentum, and energy to the boundary between proceeding and reflected wave, and also considering that in the reflected shock wave $w = 0$, it is possible to calculate p_{ref}, ρ_{ref}, T_{ref} and D_{ref} — the speed with which the boundary of additional compression is propagated. This problem was first solved by Kryussar.

Let us give, without conclusion an expression for excess pressure of reflection Δp_{ref}, inasmuch as namely this magnitude is the most important for estimating the destroying action

$$\Delta p_{\text{отр}} = (\Delta p_1 + p_0)\frac{\frac{3k-1}{k-1}(\Delta p_1 + p_0) - p_0}{(\Delta p_1 + p_0) + \frac{k+1}{k-1}p_0} - p_0. \qquad (6.29)$$

[отр = ref = reflection]

where Δp_1 is excess pressure on the front of the proceeding wave.

Considering $p_0 = 1$ kg/cm^2 and $k = 1.4$, we obtain

$$\Delta p_{\text{отр}} = (\Delta p_1 + 1)\frac{8\Delta p_1 + 7}{\Delta p_1 + 7} - 1. \qquad (6.30)$$

For very strong shock waves, when $\Delta p_1 \gg p_0$,

$$\Delta p_{\text{отр}} \approx 8\Delta p_1.$$

If one were to consider that for very strong shock waves the value of k is lowered, then in the limit

$$\Delta p_{\text{отр}} \approx (10 \div 11)\,\Delta p_1.$$

According to B. A. Olisov, the expression for Δp_{ref} may also be recorded in the following manner:

$$\Delta p_{\text{отр}} = 2\Delta p_1 + (k+1)\frac{\rho_1 w^2}{2}. \qquad (6.31)$$

Expression (6.31) is a certain approximation to the accurate expression (6.30); practically, however, they are close. Expression (6.31) is some respect is more convenient, since it graphically shows that total pressure of reflection consists, as it we, of two members: the double pressure of the proceeding wave and "wind" pressure determined by dynamic head. For weak shock waves the "wind" member does not have an essential value; in the interval for acoustical waves there occurs doubling of pressure; on the contrary, for strong waves the "wind" member is very significant. In Table 6.6 are given values for Δp_{ref} calculated by formula (6.30).

The above-considered conditions of reflections are idealized. In the calculation the following simplifying assumptions were made:

1. We assumed that the shock wave is reflected with constant values of p_1, ρ_1, T_1 after the front; the parameters of real waves after the front fall quickly.

2. We assumed that the direction of propagation of the shock wave is normal to the surface of the obstacle; in reality, fall of the wave can occur at different angles to the reflecting surface.

Table 6.6. Pressures in Reflected Shock W.ve Depending Upon Pressures in Approaching Wave (k = 1.4)

Δp_1 kg/cm^2	$\Delta p_{\text{отр}}$ kg/cm^2	Δp_1 kg/cm^2	$\Delta p_{\text{отр}}$ kg/cm^2
0,1	0,21	1,2	3,45
0,2	0,43	1,5	4,59
0,3	0,67	2,0	6,67
0,4	0,93	2,5	8,96
0,5	1,20	3,0	11,4
0,6	1,49	4,0	16,7
0,7	1,78	5,0	22,5
0,8	2,10	7,0	35,0
1,0	2,75	10,0	55,3

3. We assumed that the reflecting plane has unlimited dimensions: in reality, the barriers have finite dimensions frequently less than the length of the shock wave itself.

Let us now consider reflection of shock waves in real conditions, without the above-mentioned limitations.

Let us assume that along the surface of the earth there spreads a shock wave of the usual shape (Fig. 6.13). During passage of the shock wave, no reflections will appear, and the transducer which is fixed in the ground will register p(t) of the approaching wave; this recording is given in the upper part of Fig. 6.13. Let us assume now that this shock wave collides with a wall and is reflected (Fig. 6.14). If the transducer is set into the wall or is in the ground, but at the base of the wall, it will not register p(t) of the reflected shock wave; the corresponding recording is given in the upper part of Fig. 6.14.

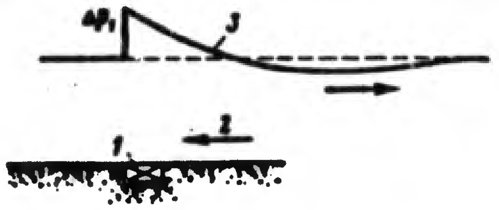

Fig. 6.13. Diagram of recording of curve p(t) in an approaching shock wave. 1) transducer; 2) direction of propagation of wave; 3) curve p(t).

As can be seen from examination of the figures, the shape of the reflected shock wave is similar to the shape of the approaching wave, only the pressure on the front is more significant and it will drop faster; the duration of compression phases of the approaching and reflected shock waves is practically identical. It is important to note the following: the earlier derived formulas (6.29)-(6.31) are valid for the front of the reflected shock wave. If consequently, we calculate the pressure of reflection, then for a real wave with lowered pressure the obtained value will be the pressure on the front of the reflected shock wave.

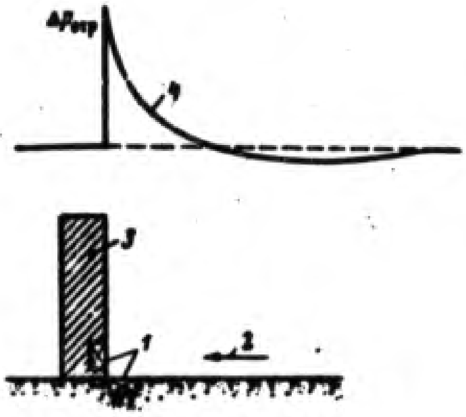

Fig. 6.14. Diagram of recording of curve p(t) in a shock wave during reflection of it from a wall. 1) transducers; 2) direction of propagation of approaching wave; 3) wall; 4) curve p(t) in reflected wave.

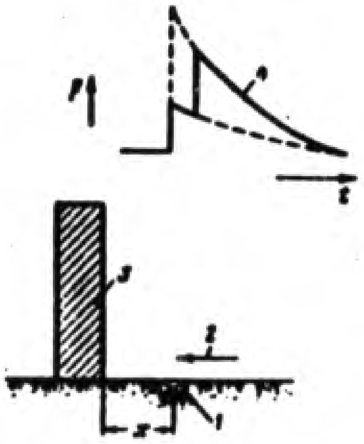

Fig. 6.15. Diagram of recording of curve p(t) during reflection of a shock wave by an instrument located a certain distance from the wall. 1) transducer; 2) direction of propagation of incident shock wave; 3) wall; 4) curve p(t) recorded by a transducer located at distance x from wall.

Fig. 6.15 shows the recording of p(t) in the case when the transducer fixed in the ground a certain distance x from the reflecting surface; the transducer at first fixes the approaching shock wave; the second peak corresponds to the arrival of the reflected shock wave at the transducer. Peak pressure then is less than Δp_{ref}

on the wall. On the same graph the dotted line shows the curve p(t) of the approaching wave and curve p(t) of the reflected wave directly at the wall. The smaller distance x, the nearer the magnitude of pressure in the second peak is to the ideal pressure of reflection.

Inasmuch as real shock waves have a final length (although it may be very significant), after a certain time the reflected shock wave will detach from the wall and will be turned into a wave which is analogous to the one approaching, but its propagation and the flow of matter in it will be directed opposite to the approaching wave, i.e., from the wall. Such a wave is also said to be reflected; in order to avoid confusion, it is perhaps better to call it a reflecting wave.

During reflection of a shock wave not only does the pressure increase, but also the magnitude of the impulse. The impulse during reflection is also possible to estimate by formula (6.12) $I = A\frac{C^{2/3}}{R}$ kg sec/m^2. In the case of trotyl, coefficient A in formula (6.21) will constitute 50-60 under the condition that C is expressed in kg and R in m. The formula for trotyl may also be used for other explosives by substituting as C the value of the trotyl equivalent.

Let us now consider reflection of a shock wave at an angle. Let us assume that at point A (Fig. 6.16) there occurs an explosion; the reflecting plane is the surface of the earth. At different points of this surface reflection occurs at different angles φ. If $\varphi = 0^\circ$, reflection is normal; if, on the contrary, $\varphi = 90^\circ$, the wave, not being reflected, slips along the surface. At small angles of incidence (points B, Ж) proceeding from the center of the explosion the shock wave И, being reflected from the surface, gives reflected wave O. If the shock wave is weak, almost acoustical, then there takes place, as it were, on optical analogy of reflection from a

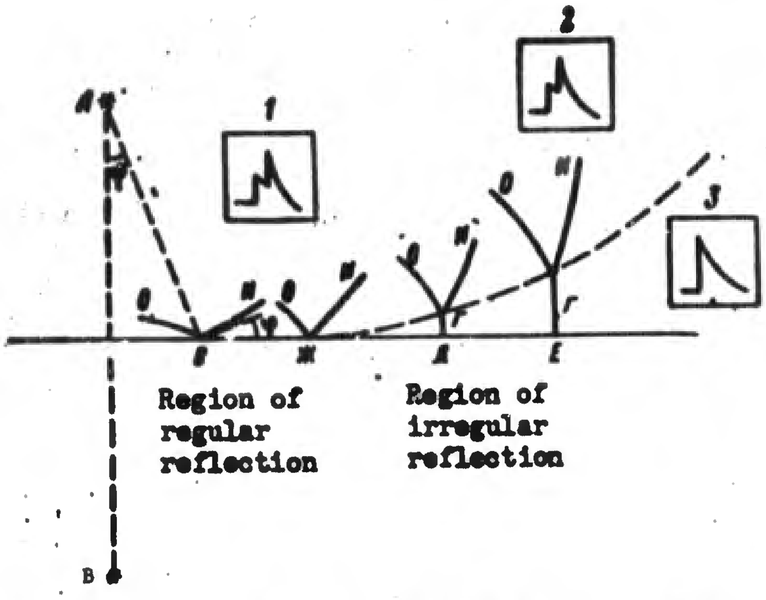

Fig. 6.16. Diagram of reflection of a shock wave falling on a plane at different angles. A) point at which explosion occurred; φ) angle of incidence of shock wave; И) front of approaching wave; O) front of reflected wave; Г) front of bow wave. 1 – curve of p(t) recorded by transducer under point B; 2 – the same, above points Д and E above dotted line; 3 – the same, above points Д and E under dotted line.

mirror and the reflected shock wave, as it were, is propagated from point Б which is a specular reflection of point A, the point of the actual explosion. If above the surface (above point B) we place the transducer, then the character of the recording will be as shown in square 1; the first peak of the recording corresponds to the approaching wave and the second to the one reflected. Such type of reflection is called regular. With increase of angle φ (point Ж) the angle between the approaching and reflected wave decreases, and correspondingly, the distance between peaks on the recording of p(t) decreases, but the general character of the recording remains as before.

Starting from a certain angle, depending on intensity of the shock wave, the character of reflection essentially changes. The reflected wave, moving through the heated air compressed by the approaching wave, is propagated normally to the front with a speed higher than the speed of the approaching shock wave. As a result, at a certain value of angle φ, part of the front of the reflected wave will overtake the approaching one. These two waves, as if merging, form a new wave, which in our literature is usually called a bow shock wave; in foreign literature it is frequently called a Mach wave. Curve p(t) for the bow wave is shown in square 3 in Fig. 6.16.

Above point Д of the surface, a triple configuration is present: the approaching И, reflected О, and bow Г shock waves, which cross in one point, called the triple point. Upon further growth of angle φ, the region enveloped by the bow wave is increased, as shown by the dotted line in Fig. 6.16. Reflection at large angles φ, when there appears a bow wave, is called irregular reflection.

With the increase of angle φ, the pressures are lowered since the wave falls at a large angle, and also because of an increase of distance. Within the limits of magnitudes of the angle from 0° to 10-20° the decrease is small and the pressure of reflection is close to ideal with normal drop. Upon further increase of the angle the pressure drops faster. In the zone of formation of the bow wave there occurs a certain relative increase of pressure especially noticeable in the case of weak waves: pressure then can be obtained larger than from a surface explosion (i.e., an explosion carried out on the surface under point A), although the distance in the last case is somewhat less.

Let us consider the interaction of a shock wave with obstacles of limited dimensions and, in particular, with an obstacle whose size is less than the extent of the shock wave. In this case there appears the phenomenon of flow around an obstacle by a shock wave. The phenomenon of flow around was established experimentally by M. A. Sadovskiy, and an elementary theory of the phenomenon was offered by Yu. B. Khariton and T. V. Zakharov.

Let us assume that the shock wave is reflected from an obstacle of limited dimensions (Fig. 6.17). In the initial moment, practically on the entire reflecting surface there appears a pressure equal to the ideal pressure of reflection (Fig. 6.17a); the region where this pressure exists borders with the region of lower pressure in the approaching shock wave. As a result, from the edges of the barrier to the middle will proceed a wave of relative rarefaction (see Fig. 6.17b), spreading with the speed of sound in compressed air. After a certain time, the wave of relative rarefaction will reach the middle of the barrier (see Fig. 6.17c) and pressure (in the middle) will drop from the value of Δp_{ref} to a certain value of Δp_{flow}. Time from the beginning of reflection to the beginning of establishment of conditions of flow around may be tentatively considered to be equal to $t = \frac{l}{c}$, where l is the distance from the edge of the barrier to the center and c is the local speed of sound.

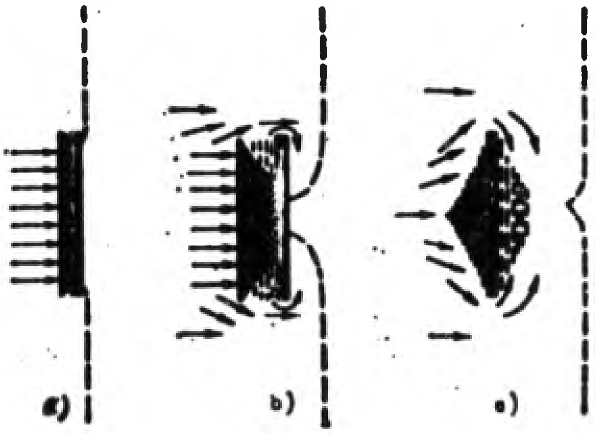

Fig. 6.17. Diagram of flow around an obstacle by a shock wave.

According to Khariton and Zakharova, after establishment of the conditions of flowing around, the pressure of flowing around for any moment of time is tentatively equal to half of the pressure of reflection

$$\Delta p_{\text{обт}} \approx \frac{1}{2} \Delta p_{\text{отр}}. \ [\text{обт} = \text{flow}] \qquad (6.32)$$

Ideal movement of the curve of p(t) in the middle of the barrier in the presence of flowing around is shown in Fig. 6.18; the dotted line in the same figure shows p(t) during reflection from an infinite barrier (presence of flowing around). In practice, the transition from reflection to flowing around does not occur in stages, but more smoothly.

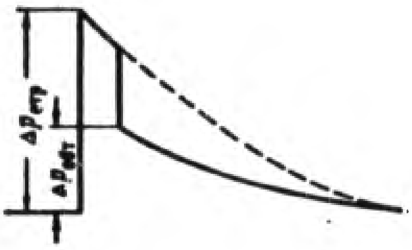

Fig. 6.18. Ideal curve of p(t) during flow around an obstacle by a shock wave.

If the size of the obstacle is not great and during the time of establishment of flowing around the drop of pressure after the front is small, then, by applying formulas (6.31) and (6.32), it is possible to estimate the magnitude of maximum pressure during flowing around:

$$\Delta p_{\text{отр}} = 2\Delta p_1 + (k+1)\frac{\rho w^2}{2};$$

inasmuch as $k + 1 \approx 2$, then

$$\Delta p_{\text{обт}} \approx {}^1/_2 \Delta p_{\text{отр}} \approx \Delta p_1 + \frac{\rho w^2}{2}. \qquad (6.33)$$

Such pressure will act on the forward, i.e., turned to the wave, area of the obstacle. After full submersion of the obstacle in the shock wave, on the rear area will act pressure of the order Δp_1. The resultant influence on the obstacle will then be equal to $\sim \frac{\rho w^2}{2}$, i.e., it will be approximately equal to the magnitude of dynamic head. Let us note that this conclusion is especially approximate.

The briefly presented question of interaction of a shock wave with obstacles have large practical and scientific value.

Thus, depending upon the conditions and situation, destruction can be determined by the following factors:

1. Excess pressure on front, impulse (or a certain part of the impulse) of the approaching shock wave.

2. Excess pressure on front, impulse or part of the impulse of the reflected shock wave.

3. Pressure, impulse or a certain part of the impulse of the flow around.

4. Dynamic head or impulse of dynamic head (or some part of it).

In the complicated conditions of interaction of shock waves with obstacles in the presence of collision of reflected shock waves, curves of p(t) can have a very complicated character. Theoretical calculation in such cases is hampered to an extreme. In such complicated conditions, the possibility of obtaining a reliable experimental recording of p(t) is especially important for a correct estimation of the destroying action.

§8. Shock Waves in Water

As a result of explosion of an explosive charge in a homogeneous aqueous medium (far from the bottom and from the surface) in the water a bubble will appear from heated compressed gases, whose pressure will be significantly higher than the pressure in the environment. In being expanded, the gases form a shock wave in the water, just as this takes place in the air. It is clear that the properties of shock waves and their characteristics should depend on the properties of the medium.

With expansion of the bubble, the pressure in it will drop quickly. At a certain moment of time the pressure in the gas bubble will be leveled with the pressure in the environment, but this will not complete the water expansion: adjoining the gas bubble, having significant speed, for some time will move by the inertia stretching the bubble. After the motion of the water ceases, the pressure in the bubble is less than the pressure in the environment, the gas bubble will start to be compressed, it will again pass the position of equilibrium and, thus, will pulsate for a certain time. Such pulsation may also be noted during an explosion in the air; however, in water, due to the large density and large forces of inertia, this phenomenon is especially prominent. The pulsating bubble starts to move upwards, as if "surfacing" in the water.

For water a comparatively high value of the speed of sound $c_0 \approx 1500$ m/sec is characteristic. The speed of the shock wave in water, decreasing with propagation, quickly attains the value of the speed of sound and the wave takes on an "acoustical" character, although the pressures in it still can be significant.

Thus, when one considers a shock wave in water with extraordinarily large pressure on the front $p_1 = 5000$ kg/cm^2, then after the front of such a wave there will be a flow of water with significant speed $w \approx 250$ m/sec. The wave will be propagated with speed $D = 1975$ m/sec, significantly exceeding the speed of sound. But if pressure on the front of the shock wave in water is lowered to a magnitude of 250 kg/cm^2, which is still very significant, then such a wave will have speed of flow after the front of only $w = 15$ m/sec and the speed of its propagation will be practically equal to the speed of sound. Since a shock wave in water quickly takes on a quasiacoustical character, and also because of other conditions of reflection on the solid surface, the effects of reflection and direction are expressed weaker than in the case of an air shock wave; the action of a shock wave in water in its character is close to the hydrostatic pressure acting equally in all directions.

Damping of shock waves in water occurs slower than in air; therefore, at identical given distances both pressure and impulse of a shock wave in water are significantly greater than in air.

Thus, for instance, the pressure of reflection in water may be approximately estimated by the formula

$$\Delta p_{отр} = \frac{530}{\bar{R}}, \qquad (6.34)$$

where $\bar{R} = \frac{R}{\sqrt[3]{C_{equ}}}$. For $\bar{R} = 2 - 3$ the pressure of reflection in water is ten times higher than the pressure of reflection in air; when $\bar{R} = 5$ the pressure of reflection in water is approximately 150-160 times more than in air.

The magnitude of the impulse of reflection of the shock wave in water may be calculated by an approximate formula

$$I \approx 930 \frac{C_{equ}^{2/3}}{R} \text{ kg sec/m}^2. \qquad (6.35)$$

Inasmuch as in air $I = 50\text{-}60 \frac{C_{equ}^{2/3}}{R}$, then at identical R and C_{equ} the impulse in water is approximately 15-20 times more than in air.

The above-mentioned formula pertained to a homogeneous aqueous medium. If the charge is not far from the surface of the water, the values of pressure and impulse can be essentially lowered.

In the explosion of a charge not far from the surface of the water, a dome will be formed on it and then ejection occurs, whereupon a water column of significant height may be formed. Research has established that formation of the dome and ejection is connected chiefly with the influence of the gas bubble.

The basic methods of research of underwater and air explosion are analogous. For research on underwater explosion it is also expedient to use the method which records p(t), especially in complicated conditions, during explosion near the surface of water, etc. For recording of p(t) they also use piezoelectric transducers; it is natural that their design differs somewhat from the air-type. Under certain conditions, for research on the behavior of the gas bubble optical methods can be used.

The question of destructive action of shock waves in water is quite complicated, especially if we speak of the action of an explosion on ships: the shock wave in the water acts on the wall, after which there is no water, but air. The theory of action of the shock wave for such cases is very complicated.

§9. Shock Waves in the Ground

Research on explosion in the ground is complicated by the fact that the structure and properties of soils (rocks) change in wide limits. Soils can be loose, plastic, or brittle; their specific gravity and especially durability are essentially different.

Specific difficulties also appear in the experimental determination of parameters of a shock wave in a solid medium. In order to characterize a shock wave in the ground, it is also necessary to know the magnitudes Δp, I, t_+, which, with the greatest reliability, can be obtained from the curve of p(t); in this case the possibility of experimental recording of p(t) is especially important: shock waves in the ground can have a somewhat unusual shape and, in particular, a sloping front. The speeds of propagation in the ground can be less than sonic.* Besides the longitudinal waves appearing in the air and in water, in a solid medium there also appear waves of transverse displacement, which are usually propagated with speeds somewhat lower than the longitudinal ones. Finally, on the interface unique surface waves appear and are propagated.

A recording of p(t) in the ground may be obtained with the help of piezo-transducers or strain gauges; however it is necessary to apply them with special attention and circumspection. With the introduction of transducers into the ground, combined with the disturbance of its continuity, with poor contact of transducers with the medium (in the case of an air or aqueous medium this contact is always ensured) the recording of p(t) may be so distorted that it will become absolutely unlike the shock wave approaching through solid ground. The enumerated difficulties, just as many others, not mentioned here, were successfully surmounted, and now there exist reliable methods of recording of p(t), especially in loose and plastic soils.

Besides parameters Δp_1, I, t_+, and also the speed of propagation of the wave D, in the conditions of the ground it is frequently very important to know the speed of displacement of the medium w and magnitude of dislocation of the medium ε. For measurement of these parameters, special instruments have been developed which are not considered here.

Let us consider an explosion in the ground of a charge, which was

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*Nonetheless, there are no foundations in this case to reject the term "shock wave;" the main criterion available is the final increase of pressure, density and other parameters in the zone enveloped by the disturbance, and also flow of matter after the front.

laid at a significant depth, so that on the surface of the ground any effects are not observed (such a charge is called a camouflet charge).

The result of the action of the explosion on the medium is usually described in three zones: the zone of displacement, the zone of destruction and the zone of concussion.

Zone of displacement (or zone of compression) – this is the region from which the products of an explosion of high pressure completely displaced the ground, having formed a cavity (so called "kettle"). Zone of destruction – this is the sphere in which, under the action of the explosion, the ground is destroyed, cracked, the bonds between particles of the medium are disturbed. Zone of concussion – this is the region in which the shock wave, propagating from the center of the explosion, is so weak that it is no longer in a state to disturb the bond between particles of ground and produces only a more or less strong concussion, weakening with propagation.

Destruction of the medium can have a different character depending upon the form of the state of stress, which is experienced by the rock in the region of action of the explosion. The fact is that rocks are significantly easier to destroy by straining than by compression, all the more so because in a solid massif the compression in a shock wave is manifold. At the same time, appearing more difficult (under higher stresses) the destruction by compression is more radical and usually has the character of continuous crushing, and then as under the action of straining there appears only a more or less thick network of cracks.

A more detailed consideration of the question of destruction of rock by an explosion leads to the conclusion (G. I. Pokrovskiy) concerning the presence of two zones of destruction distinguished according to character: the zone of crushing and the zone of breaking.

Thus, it is possible to distinguish four zones of influence of an explosion on rock: the zone of displacement, zone of crushing, zone of breaking and the zone of concussion (Fig. 6.19).

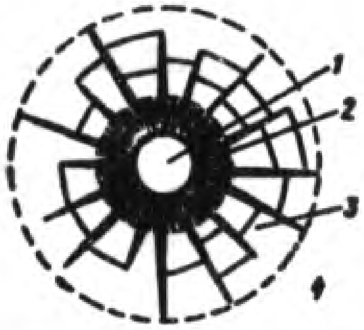

Fig. 6.19. Diagram of location of zones of coverage of explosion in the ground. 1 — zone of displacement; 2 — zone of crushing; 3 — zone of breaks; 4 — zone of concussion.

Zone of crushing — this is the zone which is pierced by surfaces of slip in which the ground is intensely broken-up and crushed as a result of the influence of a compression wave.

Zone of breaking — this is the region in which the weakened shock wave is no longer in a state to crush rock by compression. However, the matter of the medium obtains significant radial displacement (from the center of the explosion). As a result, in the medium there appear straining forces; if they exceed temporary resistance to straining, this leads to the appearance of radial cracks. Subsequent unloading prompts the formation of annular tangential cracks.

The size of every zone may be estimated according to the law of similitude. Let us assume that in the explosion of a charge weighing C in definite ground, expansion of the cavity ceases after achievement of pressure p_1 (it is clear that for various grounds the values of p_1 will be different). Inasmuch as pressure is a function of given distance (this is valid for shock waves in any media), the value of p_1 should correspond to given distance $\overline{R}_1 = \frac{R_{dis}}{\sqrt[3]{C}}$, where R_{dis} is the radius of the zone of displacement.

Let us assume further that crushing of the ground ceases when the pressure falls to the value of p_2; this pressure will correspond to given distance

$$\bar{R}_2=\frac{R_{\text{разд}}}{\sqrt[3]{C}}.$$

[разд = crush = crushing]

where R_{crush} is the radius of the zone of crushing. Analogous expressions can also be written for the other zones. From them it is easy to obtain formulas for determination of radii of corresponding zones:

$$R_{\text{выт}}=\bar{R}_1\sqrt[3]{C}; \tag{6.36}$$

[ВНТ = dis = displacement]

$$R_{\text{разд}}=\bar{R}_2\sqrt[3]{C}; \tag{6.37}$$

$$R_{\text{разр}}=\bar{R}_3\sqrt[3]{C}. \tag{6.38}$$

[разр = break = breaking]

Coefficients $\bar{R}_1$, $\bar{R}_2$, $\bar{R}_3$ are the given distances to which the values of p_1, p_2, p_3, etc, correspond for every form of ground, they must be determined by experimental means.

The action of an explosion depends not only on the properties of the ground, determining the magnitudes p_1, p_2, etc., but also on the properties of the explosive and first of all on the specific heat of explosion. Calculation of properties of the explosive is the simplest of all to produce, if as C we substitute the equivalent weight of trotyl (of high density) or the equivalent weight of ammonite No. 6.

If the values of R are given, the values of weights of the charges are determined by the formulas

$$C_{\text{сж}}=K_1R^3_{\text{сж}}; \qquad (6.39)$$

$$C_{\text{разд}}=K_2R^3_{\text{разд}}; \qquad (6.40)$$

$$C_{\text{разр}}=K_3R^3_{\text{разр}}, \qquad (6.41)$$

where

$$K_1=\frac{1}{k_1^3};\ K_2=\frac{1}{k_2^3},\ K_3=\frac{1}{k_3^3}.$$

As was noted above, the dimensions of zones depend on the properties of the ground. In plastic soils, volume of the sphere of displacement by tens and even hundreds of times (a limit of 200 times) can exceed the volume of the charge.

Until now we considered an explosion occurring deep under the earth. We now shall start to bring the charge near the surface of the ground or increase its weight. Then the zone of destruction will begin to near the surface of the earth; as a result of reflection of a shock wave from the surface of the ground the character of the influence and its effect can essentially be changed: the region will significantly increase in which shear stresses are sufficiently great for destruction, i.e., the phenomenon of plural break-away will arise. The zone where the ground is intensely split as a result of breaking will be increased very significantly and, consequently, in the end the total volume of destruction will increase. Within the limits of this course there is no possibility to remain on the theory of plural break-away in detail. Let us note only the following.

Above it was shown that when an air shock wave is reflected from a denser, in particular, a solid surface, there occurs additional compression. Essentially, otherwise there occurs reflection of the shock wave going in the solid medium, from the interface with the air. On the boundary during reflection of a compression wave there appears a wave of shearing, which starts to propagate in the opposite direction (from the plane of reflection). This wave of shearing will be algebraically added to the "tail" part of the compression wave and will give a resultant shear stress, increasing with the propagation of the reflected wave into the depth of the medium. When total stress attains a certain critical value σ_{crit} (depending on the properties of the medium), break-away will occur. The remaining part of the compression wave will be reflected from the newly formed surface, as a result of which there occurs new break-away, etc. Tentatively, the quantity of break-aways may be considered equal to $\frac{\sigma_{max}}{\sigma_{crit}}$, where σ_{max} is maximum stress on the front of the shock wave.

During reflection of a shock wave from a free surface, shear stresses great enough for breaking rock appear at a significantly larger distance from the center of the charge than in the case of an explosion in a continuous medium (charge at great depth). As a result, not only is the volume of the region of destruction essentially increased, but its form is also changed.

Let us imagine that a charge is located in the ground at distance R' from a free surface, where R' somewhat exceeds R_{break} – the radius of the zone of breaking a continuous medium in the case of an explosion far from a free surface. In the region adjoining the surface, due to reflection of the shock wave there will appear intense shear stresses, and furthermore, the motion of the medium will be facilitated (as compared to the case of deep laying of the charge) which additionally will promote the appearance of shear stresses. As a result, if in a continuous medium at distance R' the ground remains whole, then near the free surface it will be intensely destroyed. Further, if in a continuous homogeneous medium the region of destruction had the form of a sphere, then in the presence of a free surface near the focus of the explosion the region of destruction, called, in this case the loosening crater, takes on the form shown in Fig. 6.20.

Here, on the sphere (forming during an explosion in a continuous medium) is imposed a crater – the region of action of intense shear stresses combined with the presence of a free surface. In the presence of two or more free (bared) surfaces near the charge the volume of destruction will increase still more.

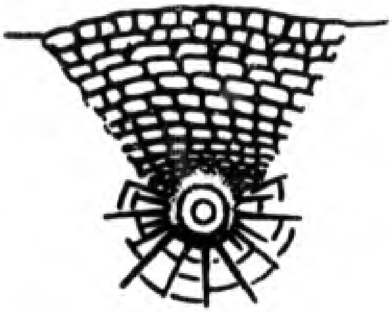

Fig. 6.20. Diagram of a loosening crater in the ground.

If a charge, forming a loosening crater (Fig. 6.20), is brought near the surface or its weight is increased, then part of the destroyed ground will be set into motion and ejected. The phenomenon of ejection is widely used in mining, construction, and so forth. The fundamentals of design of charges for ejection will be given in Chapter IX.

The shock wave is the most important factor of the destroying action of an explosion; however, in estimating destruction and splitting of a medium directly adjacent to the charge, and especially in the calculation of ejection, it is impossible to be limited only to calculation of the action of the shock wave. A very important role is played by the motion of the destroyed medium as a result of the piston action of gases of the explosion, appearing after passage of the shock wave. For the study and calculation of motion of the ground under the action of gases of explosion we shall also apply the law of similitude.

We shall now turn to elastic oscillations of the zone of concussion, which begins where destruction of the medium ends.

The totality of elastic waves in the ground is called seismic waves. They appear during earthquakes and explosions: actually, an explosion in the ground causes an artificial earthquake, propagating through a certain volume, depending on the energy given off in the explosion. The mechanism of propagation of seismic waves is significantly more complicated than the mechanism of air shock waves. It is very essentially that on the surface of the ground there appear and propagate surface waves, externally resembling waves on the surface of water, but propagating with incomparably higher speeds.

As compared to air, oscillations in the ground attenuate slower and propagate at larger distances. This especially pertains to surface waves, which even at large distances have significant amplitude and period of oscillations close to the natural period of oscillations of buildings and structures. On the seismogram of Fig. 6.21 a compression wave is fixed in the very beginning ("entry"). Subsequent oscillations of great amplitude and significant period include oscillations of the surface of the ground, arriving later, but having the highest intensity.


Fig. 6.21. Typical seismogram of an explosion.

As a result, at large distances, namely these surface waves are the most dangerous, and the most active in respect to destruction of structures on the surface of the ground. The distances at which oscillations of the ground caused by explosions become safe for buildings and structures of conventional type, can be estimated by the formula

$$R_{\text{сейсм}} = \bar{K}_s \sqrt[3]{C}. \tag{6.42}$$

[сейсм = seismic]

In Table 6.7 are given values of coefficient $\bar{K}_s$ in formula (6.42), borrowed from the "Single rules of safety while conducting explosive operations."

Table 6.7. Values of Coefficient $\bar{K}_s$ in the Formula for Calculation of Seismically Safe Distances

Form of ground on which the structure stands	Coefficient $\bar{K}_s$
Granite, gneiss	1.5
Quartzites	3.0
Limestone	5.0
Sand, dense	8.0
Humus	10.0
Freshly-poured earth	15.0
Quicksand, peat bog	20.0

Use of these coefficients assumes that the charge is detonated underground.

One should note that formula (6.42) is especially approximate and pertains to charges weighing tens, hundreds, and thousands of tons. For small charges it gives overestimated values of safe distances. Even with small sinking of the charge the air shock wave is sharply weakened, and in most cases its action as compared to seismic may be disregarded. Conversely, if the charge is located on the surface, then seismic action of the explosion is very weak and it may be ignored.

CHAPTER VII

CONTROLLING REACTIONS OF EXPLOSIVE TRANSFORMATION (THE COMPOSITION AND VOLUME OF EXPLOSION PRODUCTS)

§ 1. Methods of Determining the Composition of Explosion Products

The final result of reactions of explosive transformation is usually expressed by an equation connecting the chemical formula of the initial explosive substance or its composition (in the case of an explosive mixture) with the composition of the final explosion products. Clearly such an equation cannot give any idea of the complicated complex of elementary processes flowing in parallel and consecutively during the explosion; it gives only their final result.

A knowledge of the equation of chemical transformation during explosion is essential in two ways. On the one hand, from this equation it is possible to calculate the heat and volume of gasiform products of the explosion, and consequently also the temperature, pressure and other parameters. The methods for these calculations will be discussed in the next chapter. On the other hand, the composition of explosion products is especially important when we are talking about explosive substances intended for blastings in underground workings. In this case the explosion products get in the atmosphere of the mine and must be got rid of by ventilation of the mine. This must be calculated in such a way as to exclude the possibility of poisoning the workers. With these explosive substances, the quanity of noxious gases — carbon dioxide and nitrogen oxide — in the products of the explosion do not exceed a definite limit.

A knowledge of the formula of the explosive chemical compound or of the elementary composition of the explosive mixture still does not allow one to determine unambiguously the equation of chemical transformation during explosion.

The most accessible case for calculation occurs when the reaction during the explosion goes to the very end and chemical equilibrium is established in the products of explosion. Then, if we know the heat of formation of the explosive substance, the number of gram atoms of every element in it, and the equilibrium constants of the various reactions which can occur during explosion, it is possible to calculate the composition of the products (the quantity of gram atoms or gram moles of each of the elements and their compounds contained in the products). Calculation, however, is complicated by the fact that the equilibrium constants are known only for relatively low pressures, when the products of explosion are subject to the equation for the state of ideal gases.

In this case, if the number of moles on the right and left sides of the equation is equal, the equilibrium constant K_p depends only on temperature, and not on pressure. During an explosion of condensed explosive substances, very high pressures appear and the properties of the products, compressed to such pressures, can differ significantly from the properties of an ideal gas. It is not always possible to establish quantitatively the change in the properties of a gas and the associated divergence of the values of the equilibrium constants from the magnitudes corresponding to an ideal equilibrium, which does not depend on pressure.

Further, the equilibrium state of those reactions which accompany a change in volume depends on pressure. The pressure at the moment of explosion, especially if it has large values, can not always be determined exactly either.

Chemical equilibrium is far from being always established during an explosion. In many explosions, more frequently than was thought earlier, chemical reactions do not manage to go to the final stages corresponding to the equilibrium state. The products of explosion then contain larger or smaller quantities of intermediate compounds, through which the transformation of the explosive substance moves towards final products, but sometimes products also contain particles of unreacting explosive substance. According to Khariton's principle, the incompletion of a chemical transformation during explosion is caused by the fact that the course of a reaction takes a certain finite time, during which a sufficiently high pressure must be maintained. If the pressure drops too fast, then the course of the reactions in general, and the reactions of combustion of particles of the explosive substance in particular, is delayed even to the point where they cease altogether. The composition of the products of explosion in these conditions, when it is determined not only by the thermodynamics of equilibrium, but also in significant measure by the kinetics of chemical reactions and the gas dynamics of expansion of a substance compressed to very high pressures, is inaccessible by present calculation.

In those numerous cases when calculation does not allow us to reliably establish the final equation of explosive transformation, we naturally turn to experiment. Experimental determination of the composition of the products at the moment of explosion also encounters essential difficulties, which can be only partially surmounted. This is true even in a case when chemical equilibrium is established during the explosion. Chemical reactions occur between the compounds contained in the products of explosion, both at the stage of cooling and drop of pressure. Therefore the composition of the cold products differs more or less from the composition of the products at the moment of maximum temperature and pressure. In order to decrease this change in composition, the experiment is set in conditions in which the gasses of explosion are cooled rapidly at the expense of heat radiation or accomplishment of work. With great speed of cooling, the subsequent stages of the reactions can not occur in significant degree and the state attained at the moment of explosion, "is frozen." However, even with fast cooling, it is impossible to avoid recombination of valence-unsaturated particles (atoms and free radicals), since this happens with very great speed. Therefore, although the products of explosion at high temperatures can contain atoms and free radicals, they cannot be observed after cooling.

Thus, both calculation and experimental methods of determining the composition of the products of explosion encounter serious difficulties in a number of important cases and can give only approximate results. Below we shall consider first the methods of calculating the equations of explosive transformation and then the experimental determination of the composition of the products of explosion.

§ 2. Calculation of the Composition of the Products of Explosion

An organic explosive substance, as a rule, consists of carbon, hydrogen, oxygen and nitrogen. Consequently, the products of explosion can contain the following gasiform and solid matters: CO_2, H_2O, N_2, CO, O_2, H_2, CH_4 and other hydrocarbons, NH_3, C_2N_2, HCN, NO, N_2O, and C. If sulfur or chlorine enters in the composition of the explosive substance, then the products of explosion can contain SO_2, H_2S, HCl and Cl_2. In a case when the explosive substance contains metals (for instance Al) or their salts (for instance, nitrates, chlorates, perchlorates), then in the products of explosion we find oxides, carbonates, bicarbonates, cyanides, sulfates, sulfites, sulfides, chlorides and other compounds of metals.

In determining the composition of the products of explosion by means of calculation we divide explosive substances into two basic groups:

group I — explosives with a positive oxygen balance,

group II — explosives with a negative oxygen balance.

The oxygen balance characterizes the relation between the content of combustible elements and oxygen in the explosive. We calculate the oxygen balance usually as the difference between the quantity (weight) of oxygen contained in the explosive, and the quantity of oxygen necessary for complete oxidation of the combustible elements in its composition. The calculation is done for 100 g of explosive substance and accordingly the oxygen balance is expressed as a percentage.

If the explosive substance contains exactly as much oxygen as is necessary for complete oxidation of the combustible elements in its composition, then its oxygen balance is equal to zero. In a case when the explosive contains more oxygen than this, the oxygen balance is positive; and with a deficiency of oxygen, it is negative.

As an example, we will calculate the oxygen balance of nitroglycerine $C_3H_5(NO_3)_3$. According to the formula, a gram molecule of nitroglycerine (227 g) contains 9 gram atoms, or 144 g of oxygen. The quantity of oxygen in 100 g of nitroglycerine is

$$\frac{144 \times 100}{227} = 63,43 \text{ g.}$$

For full oxidation of 3 gram atoms of carbon and 5 gram atoms of hydrogen we require 8.5 gram atoms of oxygen or 8.5 × 16 = 136 g; for 100 g of nitroglycerine the following amount of oxygen is necessary:

$$\frac{136 \times 100}{227} = 59,91 \text{ g.}$$

The difference in the quantities of available and necessary oxygen is 63.43 - 59.91 ≅ 3.5 g; consequently, by definition, the oxygen balance is equal to +3.5%.

As a second example, we will calculate the oxygen balance of aluminum. The content of oxygen is equal to zero. For oxidation (to Al_2O_3), in 100 g of the metal we require the following quantity of oxygen:

$$\frac{48 \times 100}{54} = 88,89 \text{ g.}$$

Consequently, the oxygen balance is equal to -88.9%.

The oxygen balance is an additive characteristic of an explosive mixture; therefore it is easy to calculate this, if we know the oxygen balance of every component of the mixture. The values of the oxygen balance of the most commonly used components of explosive mixtures are given in the table in Appendix 4.

As an example using this table we will calculate the oxygen balance of safety ammonite III/1, containing 56% ammonium nitrate, 9% trotyl, 3% wood flour and 32% sodium chloride. From the table in Appendix 4, we find the value of the oxygen balance: ammonium nitrate (+20%), trotyl (-74%), and wood flour (-135%); the oxygen balance of sodium chloride is equal to zero, since it does not contain oxygen and does not require it for oxidation.

The oxygen balance of the mixture is = 0.56·20 + 0.09(-74) + + 0.03(-135) + 0.32·0 = +0.5%.

1. Calculation of the Composition of the Products of Explosion for an Explosive Substance with a Positive Oxygen Balance

(Group I)

To find the composition of the approximate equation for the explosion of an explosive substance with a positive oxygen balance we follow these simple rules; carbon is oxidized to carbon dioxide, and hydrogen to water; nitrogen and surplus oxygen are isolated in an elementary form.

We will calculate, for instance, the equation of explosion of ammatol 80/20 containing 80% ammonium nitrate and 20% trotyl. To determine the coefficients of the left side of the equation we will designate the number of moles of nitrate (molecular weight 80) as a and the number of moles of trotyl (molecular weight 227) as b. Then

$$\frac{a\cdot 80}{b\cdot 227}=\frac{80}{20};\quad a=\frac{80\cdot b\cdot 227}{20\cdot 80}=11{,}35b.$$

Taking the number of moles of trotyl as b = 1, we obtain a = 11.35. Thus, the equation for the explosion of ammatol takes the form

$$11{,}35NH_4NO_3+C_7H_5(NO_2)_3=7CO_2+25{,}2H_2O+12{,}85N_2+0{,}425O_2.$$

Experimental determination of the composition of the products of explosion of various explosive substances with positive oxygen balances shows divergences from the calculated equations in two directions. On the one hand, with a high temperature of explosion, nitrogen is partially linked with oxygen to form nitrogen oxide, and on the other hand a dissociation of carbon dioxide and water occurs; the stable products of this dissociation (carbon, hydrogen and oxygen oxides) are observed in the products of explosion.

Both these divergences, however, are weakly reflected in the composition of the products of explosion. The equilibrium concentration of nitrogen oxide even even at relatively high temperatures is comparatively small. Thus, at 1400°K it is 0.10%, at 2800°K is 4.48%, and at 3500°K is 9.23%. If we consider that the use of an explosive substance with a large positive oxygen balance is inexpedient and that, consequently, the concentration of oxygen in the products of explosion cannot be great, then not much nitrogen oxide can be formed in them.

In exactly the same way, in an explosion of a condensed explosive substance there is not an essential development of dissociation of carbon dioxide and water. The degree of dissociation, indeed, grows rapidly with temperature, since the equilibrium constants of the reactions depend on temperature

$$CO + {}^{1}/{}_{2}O_2 \rightleftarrows CO_2$$

$$H_2 + {}^{1}/{}_{2}O_2 \rightleftarrows H_2O,$$

which is depicted graphically in Fig. 7.1.

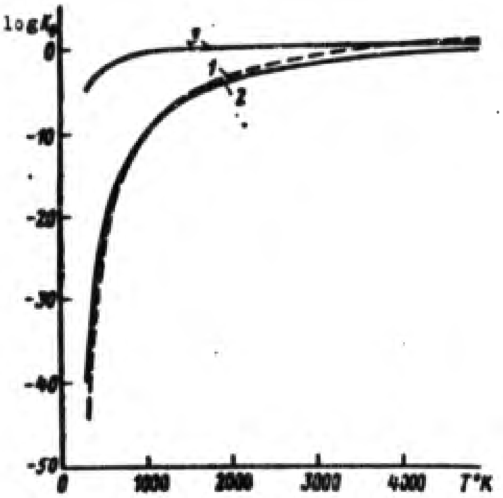

Fig. 7.1. The dependence on temperature of the equilibrium constant of the reaction of dissociation: carbon dioxide $K_p = p_{CO}p_{O_2}^{1/2}/p_{CO_2}$ (curve 1), water $K_p = p_{H_2}p_{O_2}^{1/2}/p_{H_2O}$ (curve 2), and the reaction of water gas $K_p = \frac{p_{CO}p_{H_2O}}{p_{CO_2}p_{H_2}}$ (curve 3) from temperature.

With an increase of the pressure, the degree of dissociation, however, drops sharply (Fig. 7.2 and 7.3) and at the very high pressures characteristic of explosions, dissociation is very insignificant. Therefore, during calculation of the equation of explosion we usually disregard dissociation, all the more so since calculation

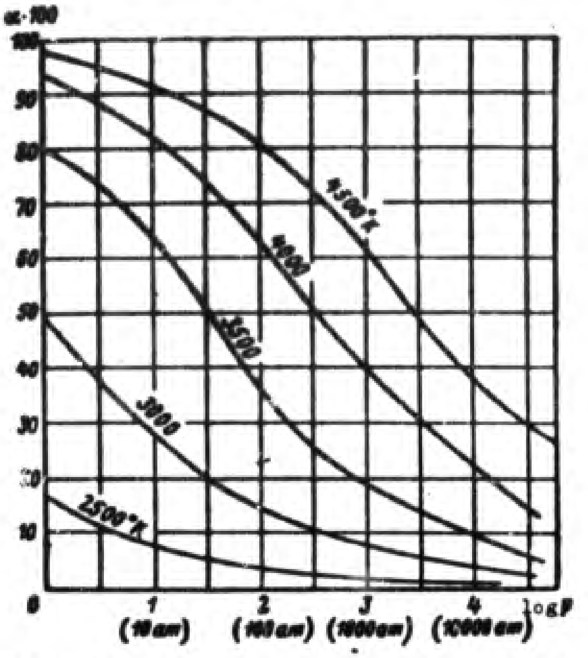

Fig. 7.2. The dependence of the degree of dissociation of carbon dioxide (α) on pressure at various temperatures (according to the calculations of Schmidt).

[*am* = at = atm (tech.)]

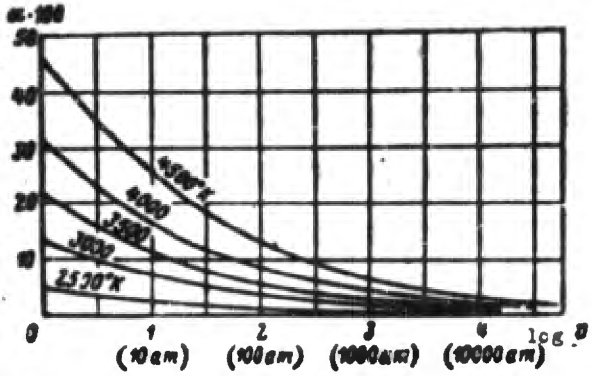

Fig. 7.3. The dependence of the degree of dissociation of steam on the pressure at various temperatures (according to the calculations of Schmidt).

of it assumes a knowledge of the pressure of explosion,* the magnitude of which at the usual high values of density of the explosive substance is not known exactly.

Experimental data confirm the validity of these conclusions. Thus, for blasting gelatine, according to Schmidt on the basis of an analysis of the products of an explosion set off by a powerful initiator, we obtain the following equation of explosion by calculation for 1 kg of explosive,

$$C_{14,13}H_{22,8}N_{12,8}O_{39,6} = 13,27CO_2 + 0,83CO + 11,17H_2O +$$
$$+ 0,17H_2 + 0,03CH_4 + 0,50NO + 0,30O_2 + 6,15N_2.$$

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*For instance, for the reaction of dissociation of carbon dioxide, according to the law of active materials, we have

$$K_p = \frac{p_{CO}p_{O_2}^{1/2}}{p_{CO_2}}.$$

Designating the degree of dissociation as α and the general pressure as p_Σ, we obtain

$$K_p = p_\Sigma^{1/2}\frac{\alpha^{3/2}}{(\alpha+2)^{1/2}(1-\alpha)}.$$

Thus, for the calculation of α, besides the magnitude of K_p, determined by the temperature, we must also know the pressure the products of explosion are under.

In spite of the high temperature of explosion (over 4000°K), the content of nitrogen oxide is only 1.5%; and the quantities of dissociated water and carbon dioxide are also small.

For explosives with a lower temperature of explosion, for instance ammonite, the influence of dissociation and the formation of nitrogen oxide is still smaller.

2. Calculation of the Composition of the Products of Explosion for an Explosive Substance with a Negative Oxygen Balance (Group II)

With respect to the method of calculation of the equation of explosion, the explosives of group II are divided into two subgroups: 1 – explosives which are completely transformed into gases and 2, explosives which form elementary carbon in the explosion. This division is somewhat conditional since the presence or absence of carbon in the explosion products depends on the pressure at which the transformation occurs. Thus, for example, nitrocellulose, burning in the form of powder in a monometric bomb, does not form carbon; upon detonation, when pressure is several dozen times greater, carbon is given off.

Subgroup 1. Explosive substances which are completely transformed into gases during explosion. The equation of transformation in this case can be approximately written as follows:*

$$C_cH_hO_oN_n = x\,CO + y\,CO_2 + z\,H_2 + u\,H_2O + \frac{n}{2}N_2.$$

The relation between the quantities of carbon monoxide, carbon dioxide, hydrogen and water is determined by the equilibrium of

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*The approximation of the equation is determined, in particular, by the fact that in it we do not consider the dissociation of molecules into atom and radicals which at high temperatures has a certain significance, especially if the pressure is low, as when combustion takes place, for instance, in a reaction chamber.

reaction of water gas

$$CO+H_2O\rightleftarrows CO_2+H_2+9850\ \text{cal}^*.$$

Since the number of moles of gases on the right and left sides of the equation is equal, this equilibrium does not depend on pressure or on the density of the explosive substance and this greatly facilitates calculation and makes the results more reliable. Furthermore, because of the comparatively small thermal effect of the reaction of water gas, the equilibrium constant grows relatively slowly with an increase of temperature (see Fig. 7.1 or Appendix 7) and this also simplifies calculation.

Equating the number of atoms of separate elements on the right and left sides of the equation, we obtain

$$x=c-y;$$
$$u=o-(c-y)-2y=o-c-y;$$
$$z={}^1/_2h-u={}^1/_2h-o+y+c.$$

From the expression of the equilibrium constant we get

$$K_p=\frac{ux}{zy},$$

or

$$K_p=\frac{(o-c-cy)(c-y)}{({}^1/_2h-o+y+c)y}.$$

Thus, for determination of the four magnitudes x, y, z and u, we have a system of four equations. They can be reduced to a quadratic equation with respect to y:

$$ay^2+by+C=0$$

or

$$(K-1)y^2+[K({}^1/_2h-o+c)+o]y+c\ \ c-o)=0,$$

whence

$$y=\frac{-[K({}^1/_2h-o+c)+o]\pm\sqrt{[K({}^1/_2h-o+c)+o]^2-4(K-1)c(c-o)}}{2(K-1)}.$$

Calculating y, we easily determine the values of x, u, and z.

As an example we will calculate the equation of explosive

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*Thermal effect at 18°C.

transformation of:

$$C_{24}H_{32}O_{36}N_8 = xCO + yCO_2 + zH_2 + uH_2O + 4N_2.$$

The unknowns x, y, z, and u are related by the following obvious equations

$$x + y = 24;$$
$$2z + 2u = 32;$$
$$x + 2y + u = 36.$$

Let us assume that the temperature of explosion for the (moment unknown)* is equal to 2900°K.

According to the table in Appendix 7, for this temperature $K_p =$ = 6.95. Then we can write

$$\frac{[CO][H_2O]}{[CO_2][H_2]} = 6{,}95$$

or in our symbols

$$\frac{xu}{yz} = 6{,}95.$$

After elementary transformations this system is reduced to a quadratic equation with respect to y:

$$5{,}95y^2 + 63{,}8y + 288 = 0.$$

The root of this equation (it is obvious that only the positive root has physical meaning) is y = 3.42 whence we easily find

$$x = 20{,}58; \quad z = 7{,}42; \quad u = 8{,}58.$$

The equation of explosive transformation has the following form

$$C_{24}H_{32}O_{36}N_8 = 20{,}58CO + 3{,}42CO_2 + 7{,}42H_2 + 8{,}58H_2O + 4N_2.$$

If we know the final composition of the reaction, it is possible to calculate the heat of explosive transformation and the temperature (see Chapter VIII). If in our addition we obtain that temperature which was set during the calculation, then the calculation of the equation was done correctly. Otherwise it is necessary to repeat the calculating, setting another temperature.

During the calculation we assumed that the equilibrium of the reaction of water gas depends only on the temperature. This

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*For the method of preliminary estimation of the temperature of explosion, see Chapter VIII.

assumption is correct only in a case when the pressure is not too great. When the pressure is great in the expression of the equilibrium constant we should not use the partial pressures of the reagents, but their <u>fugacity</u>. Fugacity is by definition those characteristic of gases, with which when they are substituted for partial pressures in the expression of the equilibrium constant the expression retains its significance even at high pressures. The methods of calculation of fugacity vary: The majority are useful only for not too great pressures, smaller than the usual pressures of detonation.

One of these methods consists of the following.

The relation of the fugacity of a gas to its partial pressure is called the <u>activity coefficient</u>. By definition

$$\gamma_i = \frac{f_i}{p_i}, \tag{7.1}$$

where γ_i, f_i and p_i – are the activity coefficient, the fugacity and the partical pressure of the i-th component of the gas mixture, respectively.

As has been proved in courses of thermodynamics,

$$\lg \gamma = -\lg \frac{1}{RT} \int_0^p a\,dp, \tag{7.2}$$

where $a = v_{ideal} - v_{real} = RT\text{-}pv/p$.

It is easy to show that

$$\lg \gamma = -\frac{1}{RT} \int_0^p \frac{RT - pv}{p}\,dp = \int_v^\infty \frac{1 - \frac{pv}{RT}}{p} \left(\frac{dp}{dv}\right)_T dv. \tag{7.2a}$$

Substituting in the expression of the equilibrium constant of water gas the pressures at fugacity, taking into account (7.1) we have

$$\frac{\gamma_{CO}p_{CO}\gamma_{H_2O}p_{H_2O}}{\gamma_{CO_2}p_{CO_2}\gamma_{H_2}p_{H_2}} = K_p, \qquad (7.3)$$

or

$$\frac{p_{CO}p_{H_2O}}{p_{CO_2}p_{H_2}} = K_p\frac{\gamma_{CO_2}\gamma_{H_2}}{\gamma_{CO}\gamma_{H_2O}}.$$

Designating $\frac{\gamma_{CO_2}\gamma_{H_2}}{\gamma_{CO}\gamma_{H_2O}}$ as G, we obtain

$$\frac{p_{CO}p_{H_2O}}{p_{CO_2}p_{H_2}} = K_pG. \qquad (7.4)$$

The activity coefficient of each of the gases may be calculated from the expression (7.2) or (7.2a) and the equation of state used for high pressures.

If we know the activity coefficients of each of the gases, it is possible to calculate the correction factor G, in the equation (7.4). Rough estimation of the composition of the products of explosion, taking into account the nonideality of gases, will be considered in the following chapter, in connection with calculation of the pressure during the explosion.

To the substances of the first subgroup of group II contemporary smokeless powders belong. At the pressures of a gun barrel, calculation of the composition of the products of combustion may be performed as described above. If it is necessary to calculate the composition of the products of combustion in a rocket chamber, where the pressure is usually much lower and sometimes does not exceed 100 atmospheres, then we must take into account the dissociation of different gases. The role of dissociation is increased, if we are speaking of a powder with high combustion heat.

It is possible to calculate dissociation if, not limiting ourselves to calculation of the equilibrium of the reaction of water gas, we solve at the same time the equations of equilibrium of the following reactions; the constants of these are given in Appendix 7 (p. 815).

$O_2 + O \rightleftarrows O_3$

$C + {}^1/_2 O_2 \rightleftarrows CO$

$2O \rightleftarrows O_2$

$2N \rightleftarrows N_2$

$2H \rightleftarrows H_2$

$CO + {}^1/_2 O_2 \rightleftarrows CO_2$

$OH + {}^1/_2 H_2 \rightleftarrows H_2O$

$H_2 + {}^1/_2 O_2 \rightleftarrows H_2O$

$NO + {}^1/_2 O_2 \rightleftarrows NO_2$

$NO \rightleftarrows {}^1/_2 O_2 + {}^1/_2 N_2$

Of these reactions the processes leading to the formation of hydroxyl, atomic hydrogen and oxygen, molecular oxygen and hydrogen and nitrogen oxide, have a predominant influence on the composition of the products of combustion. According to the calculations of Uimpress, the composition of gases, which is obtained as a result of combustion of typical high calorie nitroglycerine powder at a pressure of 10 at and a temperature of 3300°C, in percentages, in volume, is the following: CO_2 – 9.4; CO – 33.6; H_2O – 13.8; N_2 – 11.9; H_2 – 6.3; O_2 – 3.2; O – 3.6; NO – 1.4; N – 0.2; H – 6.0; OH – 10.6. At 100 at and the same temperature, the contents are: hydroxyl 6.1%, atomic hydrogen 1.7%, atomic oxygen 0.7% and molecular oxygen 1.3%.

Subgroup 2. Explosives whose oxygen content is insufficient for full transformation of all the combustible elements into gasses. In this case part of the carbon contained in the explosive substance is given off in an elementary form.

It is possible to calculate the quantity of carbon which is given off on the basis of the following considerations. It is obvious that the more carbon is contained in the explosive, the more CO should be obtained and the less CO_2. However, the ratio CO/CO_2 cannot exceed a certain maximum, which is determined by the equilibrium of the so-called reaction of blast furnace gas

$$CO \rightleftarrows {}^1/_2 CO_2 + {}^1/_2 C + 20375 \text{ cal},$$

depending on the pressure and on the temperature.
If the CO/CO_2 ratio becomes larger than is allowed by this equilibrium, then the CO portion turns into CO_2 and carbon is given off. The higher the pressure, the lower at a given temperature is maximum equilibrium concentration of CO. In accordance with this, experiments will show that with a large density of the explosive, the CO/CO_2 ratio in the products of explosion decreases.

Thus, for picric acid at $\rho = 1.0$, the ratio is $CO/CO_2 = 4$; and for $\rho = 1.5$ the ratio is $CO/CO_2 = 1.3$.

The equilibrium constant of the reaction of blast furnace gas may be expressed as the partial pressures in the following form

$$K_p = \frac{p_{CO}}{p_{CO_2}^{1/2}}. \qquad (7.5)$$

Its dependence on temperature is depicted on the graph of Fig. 7.4.

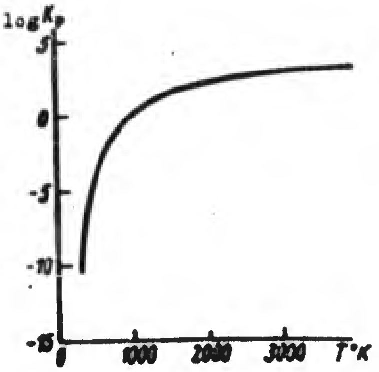

Fig. 7.4. The dependence of the equilibrium constant of the reaction of blast furnace gas ($K_p = p_{CO}/p_{CO_2}^{1/2}$) on temperature.

In turn, the partial pressures can be expressed by the overall pressure and volume percentage of the given gas in the composition of the mixture:

$$p_{CO} = \frac{p_\Sigma(\%CO)}{100}$$

and

$$p_{CO_2} = \frac{p_\Sigma(\%CO_2)}{100},$$

where p_Σ — overall pressure.

Placing these values in the equation (7.5), we obtain

$$\frac{[\%CO]^2}{[\%CO_2]} = K_p^2 \frac{100}{p_\Sigma}. \qquad (7.6)$$

Since K_p increases with temperature, the content of carbon monoxide grows with temperature and, as we can see from formula (7.6), drops with pressure.

Calculation of the equation of explosive transformation may be done in the following form. We will assume that the formula of the explosive $C_cH_hO_oN_n$. The equation of explosive transformation is calculated, as for a substance of subgroup 1, i.e., taking into account only the equilibrium of the reaction of water gas. On the basis of the results of the calculation we calculate the percentage of CO and CO_2 in the composition of the products of explosion. We put these magnitudes in equation (7.6), setting a tentative temperature and pressure of explosive transformation. If the left side of equation (7.6) turns out to be less or equal to the right side, then carbon will not be given off. If, however,

$$\frac{[\%CO]^2}{[CO_2]} > K_p^2 \frac{100}{p_\Sigma},$$

then part of the carbon will be given off in elementary form. We will assume that α gram atoms of carbon will be given off. Then we can write the formula for transformation into gases of part of the substance in the form $C_{c-\alpha}H_hO_oN_n$.

For this formula we repeat the calculation with respect to the equilibrium of the reaction of water gas. We check again, the composition of gases that we obtain by the equilibrium of the reaction of blast furnace gas (7.6). It is obvious that the content of carbon monoxide now will be less than in the initial calculation, and the left side of the equation will decrease. If the left side is still larger than the right, then we set a larger value for α and repeat the calculation. The subsequent approximations are continued until the left side becomes equal to the right.

Thus, calculation of the composition of the products of explosion with a yield of elementary carbon is possible in principle. It is not, however, recommended for practical determination of the equation of the explosion. On the one hand, in order to calculate the influence of the equilibrium of the reaction of blast furnace gas, it is necessary to know the pressure of the explosion, which is usually precisely the unknown. On the other – hard carbon in the composition of the products of explosion, as a rule, is accompanied by carbon and nitrogen compound, (the formation of which we did not consider above), acetylene, cyanogen, prussic acid, ammonia, etc. Calculation of the corresponding equilibrium reactions, which is in principle possible, would lead to extraordinarily cumbersome calculations, which are practical only with electronic computers. In this case we usually avoid theoretical calculation of the equation of explosion and resort to experimental determination of the composition of the explosion products. Nonetheless, these calculations retain their interest, since they allow us to obtain an approximate idea of the composition of the products of explosion and, without making the calculations, to exclude clearly incorrect equations of explosive transformation sometimes given in the literature.

Thus, for instance, for picric acid one author has given the following equation of disintegration

$$8C_6H_2(NO_2)_3OH = 28CO + 6CH_4 + 12N_2 + 7C_2,$$

this is evidently incorrect, since in the presence of carbon and carbon monoxide the products of explosion should also contain carbon dioxide, not to speak of the absence of hydrogen and water in the equation.

The equation of explosion of hexogene, given by another author, is also erroneous

$$C_3H_6N_6O_6 = 3CO + 3H_2O + 3N_2,$$

this does not include hydrogen and carbon dioxide, which must be formed in conformity with the equilibrium of the reaction of water gas.

§ 3. Experimental Methods of Determination of the Composition of the Products of Explosion

1. General Characteristics of the Methods and Equipment

For experimental determination of the composition of the products of explosive transformation, we use basically two instruments, the manometric bomb, when we talk about burning an explosive substance under high pressures, and the Bikhelya type of bomb for determination of the composition of products of detonation.

The manometric bomb is a thick-walled steel tube, closed at both ends by screwed in steel stoppers. Since the basic purpose of the bomb is determination of the pressure during combustion in a closed space, a detailed description of it will be given in Chapter VIII, see p. 639). Two factors are essential for us now: the presence in the bomb of a valve, allowing us to remove a sample of the products of combustion after the experiment, and the small volume of the bomb (usually 22 cm^3, maximum 200 cm^3), which does not allow us to carry out in it the detonation of an explosive requiring a capsule-detonator for its excitation.

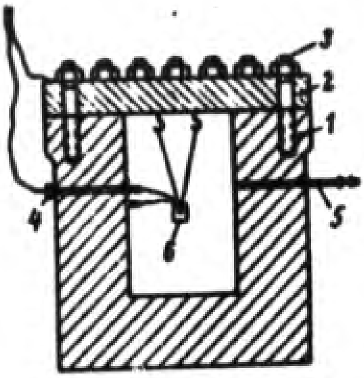

Fig. 7.5. The arrangement of the Bikhelya bomb. 1 — body of the bomb; 2 — cover; 3 — bolts; 4 — electronisolated input; 5 — valve for evacuation of the bomb and selection of gases after the explosion; 6 — charge explosive substance.

Experiments in the manometric bomb are usually made at a density of loading, not exceeding 0.5 kg/1 that corresponds to a maximum pressure near 4000 kg/cm^2. In bombs of greater durability it is possible to conduct experiments at pressures reaching 6000 kg/cm^2.

The Bikhelya*Bomb (Fig. 7.5) is a thick-walled steel vessel with an internal diameter 20 cm, and volume near 20 1, which is hermetically sealed by a cover. In the wall or cover of the bomb is an electronisolated rod, to which is joined the conductor of an electro-detonator. Another conductor is joined to the body of the bomb. The explosion of the electro-detonator evokes the detonation of the charge of the explosive being tested. Before the experiment, as a rule, the air is pumped from the bomb (to a residual pressure of 50 mm in the mercury column, or less). Otherwise the air remaining in the bomb is able to react with the products of explosion, and to essentially change their composition. The charge of explosive (usually 100 g) in a factory or

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*The bomb of B. E. Dolgov is a variant of the Bikhelya bomb; the chief distinction of this variant consists in its larger volume (50 liter).

standard paper shell is suspended in the center of the bomb and produces the explosion. The bomb and the products of explosion in it are cooled to room temperature, after which the pressure in the bomb is measured. If we know the temperature T of the bomb at the moment of rest, the measured pressure p of the products of explosion, the volume of the bomb v, and the pressure of saturated steam at a temperature T, which is equal to p_{H_2O}, we can calculate the volume of gases (without water) in normal conditions, formed by one kilogram of explosive

$$v_0 = \frac{v(p - p_{H_2O}) \cdot 273 \cdot 1000}{760T \cdot q},$$

where q – the weight of the detonated charge in g.

Removing the sample of gas with the help of the valve in the bomb and analyzing it by the usual methods, we determine the content of various gases, entering into the composition of the products of explosion. The quantity of water formed during the explosion of an organic explosive substance containing oxygen is established by subtraction, since it is not determined during the usual gas analysis. It can also be determined by passing dried air through the bomb and absorbing the water in a tube with calcium chloride or other desicant. On the basis of the gas analysis we set up the equation of explosion, taking into account the air remaining in bomb, the oxygen in which, in the case of an explosive with a negative oxygen balance, participates in the reaction.

For explosives used in underground works, we also calculate, the conditional total volume of poisonous gases, formed by 1 kg of explosive. For that, we add to the volume of carbon monoxide ten times the volume of nitrogen oxides ($NO + NO_2$). This principle of calculation, however, is not entirely well founded since in the first place, it assumes that the toxic effect of carbon monoxide and nitrogen oxides can be added together though in general, this does not occur, and, secondly, it comes from an exaggerated 10:1 ratio between the toxicity of nitrogen oxides and carbon monoxide.* With underground explosives the volume of poisonous gases determined by this method must not exceed 50 l to 1 kg of explosive.

2. Experimental Data

The initial study of the composition of the products of explosion was done exclusively with the aid of the manometric bomb. In this way Nobel and Abel investigated samples of black powder of varying composition. They established that with an increase in the density of the charge, and consequently in the pressure under which combustion occurs, the ratio CO_2/CO increases.

Analogous results were obtained by Sarro and Viel during the study of the combustion of picric acid. Experiments were set up at different densities of the charge in a platinum plated interior of the bomb, filled with nitrogen. The results of these are given in Table 7.1. They show that with an increase in the density of the charge the quantity of CO_2 increases, and the quantity of CO decreases in qualitative correspondence with the requirements of the equilibrium of the reaction of blast furnace gas. Simultaneously with the increase of the content of CO_2 a significant increase in the quantity of methane is observed.

The question of the stage of the explosion at which methane is formed has been the subject of important discussion. The fact is that directly after combustion or explosion, the gasiform products have a high temperature and pressure. In these conditions the speed of

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*Therefore recently the conversion factor 6.5:1 has been used.

Table 7.1. The Dependence on Density of the Charge of the Composition of Gasiform Combustion of Picric Acid (According to Sarro and V'el)

Gases (without H_2O)	Content of gas in % by volume		
	Density of charge Δ in kg/l		
	0,1	0,3	0,5
CO_2	7,61	15,40	20,55
CO	61,56	54,31	48,80
CH_4	1,19	5,75	7,63
H_2	12,52	6,31	3,06
N_2	17,12	18,20	19,76

chemical reactions is great. Later the gases are cooled at the expense of heat radiation in the environment or expansion, with the accomplishment of work. If this cooling does not occur too fast, chemical reactions between the initial products can occur up to a point and therefore the composition of the cooled gases differs more or less from their composition at the moment of explosion.

What we have said may be clarified by an example of an explosion stoichiometric mixture of hydrogen with oxygen at atmospheric pressure. It is known that as a result of such an explosion hydrogen and oxygen are completely turned into water. At the same time it has been proven that at high temperature and relatively low pressure, at the moment of explosion, the products of this contain, in addition to water, much molecular hydrogen and oxygen, hydroxyl, and even atomic hydrogen, which are transformed into water only upon cooling.

A similar phenomenon occurs in a case of combustion or explosion of a condensed explosive substance the study of this was initially carried out in connection with the observation of methane during the analysis of the products of explosion in a manometric bomb of an explosive with a negative oxygen balance. Sarro and V'el explained the formation of methane during an explosion of picric acid by the reactions

$$CO + H_2 \rightleftarrows \tfrac{1}{2}CO_2 + \tfrac{1}{2}CH_4$$

and

$$CO + 3H_2 \rightleftarrows H_2O + CH_4$$

occuring at the moment of explosion.

Poppenberg and Stefan, on the contrary, considered that methane was formed not at the moment of explosion, but during secondary reactions, occurring during the cooling of the gases in the bomb. In confirmation of this they pointed out the constancy of the relation $\frac{[CO][H_2O]}{[CO_2][H_2]}$ in the composition of the gases, i.e., the equilibrium constant of the reaction of water gas, observed during experiments in the bomb for explosive substances and powders very different in composition and temperature of explosion with the same density of charge.

They explained this constancy in the following way. The temperature of the gases drops at the expense of heat radiation to the walls of the bomb. The equilibrium constant of the reaction of water gas decreases correspondingly. At the beginning, when the temperature is still high and the speed of reaction is great, in accordance with the change of constant, the composition of the gases can change. However, when a certain temperature is reached, the speed of reaction becomes so small that a change in the composition of the gases ceases to follow a further lowering of temperature — the equilibrium "is frozen." Therefore as a result of the experiment in the bomb we obtain the composition of the gases, which corresponds not to the maximum temperature reached in combustion or explosion, but to the temperature "of the freezing" of the equilibrium. It was impossible to resolve this problem theoretically. On the one hand, it seemed impossible for methane to be formed at the moment of explosion, since at high temperatures it is unstable. Thus, according to Berthelot, methane decomposes during heating in a quartz vessel to 1300°C; according to Mayer and Altmayer, who investigated the equilibrium,

$$C + 2H_2 \rightleftarrows CH_4$$

this reaction gives almost exactly one methane at temperatures higher than 250°; at 850° and 1 at the content of methane is only 1.5%. These facts, however, do not exclude the possibility of formation of methane even at significantly higher temperatures, if we take into account the high pressures appearing in the bomb as a result of combustion or explosion. An increase of pressure displaces the equilibrium in the direction of the formation of methane.

For clarification of the mechanism of formation of methane experiments were also set up in which, in one case, the bomb was in boiling water, and in the other case it was in liquid air. In the latter case the cooling of the gases occurred significantly faster and the quantity of methane was significantly lower. Analogous experiments were performed by Mürauer with powders. The powder was burned in an erosion bomb so that the gases could be rapidly cooled, expanding as they flowed out of the bomb. These experiments confirmed the idea that methane is formed during secondary reactions, it is possible for them to occur to a significant degree.

Finally, the question was still more definitely solved by the experiments, set up by Poppenberg and Stefan. A charge of pressed picric acid was placed in a Trautsly lead bomb, covered by a lead disc, with sand packing with a second lead disc over it. The lead bomb was placed in an evacuated steel bomb and an explosion was produced. The products were cooled very fast at the expense of accomplishment of work by the expansion of the lead bomb, and equilibrium "froze" with a composition of gases close to that which took place at the moment of explosion. In spite of the great density of the charge of picric acid, the content of methane in the products, obtained in this experiment was only 0.5% whereas in a manometric bomb with a significantly smaller density (0.5 kg/l) Sarro and V'el obtained nearly 8% methane.

Thus, the methane, observed during experiments in a manometric bomb, is formed not at the moment of attainment of the maximum pressure, but during the subsequent cooling. Since during cooling the proportions of the other component products also change analysis, the cooled products of combustion or explosion in the manometric bomb does not reflect their initial composition.

To delay the course of reactions occurring during cooling, it is possible to carry out an explosion in conditions of accomplishment of work by the expanding products. Since work is done rapidly, cooling occurs so fast that no significant displacement of the equilibrium occurs. One of the methods founded on this principle is that described above, blasting the explosive substance in a Trautsly bomb, placed in turn in an evacuated space.

Another method of fast cooling of the products of explosion is based on the location of the charge of explosive in a liner of dry fine-grained inert material, for instance, quartz sand. The gases, formed during explosion, in expanding, penetrate through the liner, come in contact with the material over a large area and are rapidly cooled. This interrupts the course of the chemical reactions in the products of explosion. Experiments show, however, that in these conditions the development of chemical reactions can be delayed so much that chemical equilibrium in general is not attained. Then in the products we observed primary and intermediate compounds, formed in the course of combustion of particles upon detonated transformation, and also, sometimes, particles of unreacting explosive substance.

In the light of what we have said, experimental determination of the composition of the products of explosion, even in case of a chemically uniform explosive substance, presents a sufficiently complicated problem, since this composition is not a simple characteristic of the explosive substance, but changes depending upon the conditions of explosion.

In unfavorable conditions, for instance with a small diameter of the charge or a coarse-grained structure of the explosive, the scattering of the initial substance during the explosion is relatively great and, if cooling occurs rapidly, the transformation does not reach chemical equilibrium.

If the conditions for the course of the reactions are favorable, and scattering of the explosive substance is impeded (for instance, in the presence of a solid metallic liner), then the transformation takes place more fully and equilibrium can be attained. If the subsequent cooling occurs sufficiently fast (for instance, during explosion of a small charge in a large space, i.e., with a large cooling surface), equilibrium will not be essentially displaced, especially if the final pressure, and consequently also the speed of reactions are small.

Equilibrium is also attained in a case when the explosive is detonated without a liner, but cooling occurs slowly, for instance during an explosion of the charge in an evacuated bomb, where expansion occurs without the accomplishment of work and gases maintain a high temperature for a sufficient time. Then the reaction goes to the end and particles of explosive or products of incomplete transformation, are not observed. However, in this case equilibrium corresponds to low pressure. Completion of the reactions here can also be promoted by a great increase in the temperature and pressure of the expanding gases upon their encounter with the walls of the bomb. Due to suppression of the movement of the gases, their kinetic energy is transformed into heat.

Finally, if the process takes palce with large densities of the charge and conditions of slow cooling, as this occurs, for instance, in the manometric bomb, then equilibrium not only is attained, but it is displaced during subsequent cooling. This displacement takes place in a direction which corresponds to lower temperatures, but comparatively high pressures, determined by the density of the charge used.

Differences in the composition of the products of explosion are observed not only under laboratory measurement, but also in conditions of practical application. The formation of the poisonous gases (NO and CO) in explosion of ammonite depends greatly on the possibility of fast cooling of the products of explosion in the early stages of chemical transformation before chemical equilibrium is attained. Cooling delays the reduction of NO to nitrogen and oxidation of CO to carbon dioxide.

Experimental research on the composition of the products of explosion is done by different methods.

By the method of explosion of a small charge of explosive in a lead bomb, placed in an evacuated space. Schmidt determined the composition of the products of explosion of a number of explosive substances with different densities and conditions of detonation. In these experiments the old blasting gelatine, which as significantly lost its original great sensitivity to detonation, was detonated with a relatively weak capsule-detonator (a charge of 2 g of slightly pressed lead azide) and stronger (0.3 g lead azide and 1 g PETN). In the latter case, in the authors opinion, maximum speed of detonation is attained more rapidly and correspondingly explosion passes occur during higher average pressure. The composition of the products of explosion (on 1 kg of explosive) in the first and second cases may be expressed by the number of moles, given in Table 7.2. In the case of blasting gelatine the composition of the gases changes almost not at all, because at close to zero oxygen balance the composition of the products does not depend essentially on the pressure.

In exactly the same way, does not change with a change of the initial impulse the composition of the products of explosion PETN. In this case, the composition of the gases is determined mainly by the equilibrium of the reaction of water gas, on which pressure does not have any great influence.

For an explosive with a strongly negative oxygen balance, for instance trotyl, the equation of explosion depends on the reaction of blast furnace, gas and the composition of the products (see Table 7.2) is changed with a transition from a weak to a strong initiator. This change occurs in the direction corresponding to an increase of pressure, the equilibrium of this reaction is displaced in the direction of an increase in the quantities of free carbon and carbon dioxide.

With an identical strong impulse, the pressure of the explosion depends on the density of the charge; the composition of the products of explosion of picric acid and tetryl, therefore changes with density, as can be seen from Table 7.2.

Table 7.2. The Composition of the Products of Explosion of a Certain Explosive Substance in Varying Conditions of Initiation and Density ρ (According to Schmidt)

The explosive and its formula (for 1 kg)	Conditions of explosion	Composition of the products of explosion in g-mol/kg												
		C	CO_2	CO	H_2O	H_2	CH_4	C_mH_n	NO	O_2	N_2	HCN	C_2N_2	NH_3
Blasting gelatine $C_{14.1}H_{22.8}O_{39.64}N_{12.8}$	Weak impulse ρ = 1.45 kg/liter	–	13.09	0.98	11.13	0.21	0.03	–	0.70	0.15	6.05	–	–	–
	Strong impulse ρ = 1.45 kg/liter	–	13.27	0.83	11.17	0.17	0.03	–	0.50	0.30	6.15	–	–	–
PETN $C_{15.82}H_{25.31}O_{37.96}N_{12.65}$	Weak impulse ρ = 1.54 kg/liter	–	9.18	6.64	10.97	1.69	–	–	1.32	0.36	5.67	–	–	–
	Strong impulse ρ = 1.54 kg/liter	–	9.34	6.44	11.05	1.53	–	–	1.0	0.40	5.82	–	–	–
Nitrocellulose (13.3% N) $C_{21.1}H_{25.4}O_{36.6}N_{9.6}$	Weak impulse ρ = 0.3 kg/liter	0.5	7.74	12.58	8.40	4.14	0.05	0.03	–	0.07	4.81	–	–	–
	Strong impulse ρ = 1.3 kg/liter	2.5	8.05	10.29	9.93	2.45	0.15	–	–	0.14	4.81	–	–	–
Tetryl $C_{24.4}H_{17.4}O_{27.9}N_{17.4}$	Strong impulse ρ ≈ 0.9 kg/liter	0.3	3.02	18.83	3.03	3.64	0.48	0.02	–	–	7.73	1.2	0.2	0.3
	Strong impulse ρ = 1.56 kg/liter	5.8	5.59	10.85	5.91	1.89	0.27	0.03	–	–	7.82	0.6	0.58	–
Picric acid $C_{26.2}H_{13.1}O_{30.6}N_{13.1}$	Strong impulse ρ ≈ 1.0 kg/liter	0.8	4.49	17.6	4.02	1.70	0.16	0.04	–	–	5.02	0.66	1.22	0.1
	Strong impulse ρ = 1.45 kg/liter	6.8	7.88	10.18	4.60	1.08	0.12	0.01	–	–	5.81	0.33	0.4	0.3
Trotyl $C_{30.8}H_{22.0}O_{26.4}N_{13.2}$	Weak impulse ρ = 1.52 kg/liter	6.6	1.78	18.63	4.25	5.34	0.10	0.09	–	–	4.74	1.1	1.2	0.3
	Strong impulse ρ = 1.52 kg/liter	15	5.30	8.79	7.05	1.69	0.03	0.05	–	–	5.2	1.4	0.1	0.9

The data in Table 7.2 refer to a case when chemical equilibrium is displaced during cooling.

With the second method — the explosion of the charge in a liner of inert powder — the composition of the products differs essentially from the corresponding equilibrium.

Little research is done with this method on individual explosives. According to Apin, during an explosion of nitroglycerine in a test tube, surrounded by quartz sand, significant quantities of nitrogen oxide are formed, form 3 to 11%, whereas without sand, nitrogen oxide is not generally obtained.

In Table 7.3 the composition of the gasiform products of an explosion of macrocrystalline tetryl is given according to this researcher. Besides the change in the composition of the gases, during an explosion in sand the quantity of hard residuum increases and the general volume of gasiform products decreases correspondingly.

Table 7.3. The Composition of the Products of Tetrly (According to Apin)

Products of explosion	Content of components of products in % by volume	
	Charge is freely suspended in bomb	Charge is surrounded by quartz sand
CO	52,90	46,36
CO_2	8,61	14,55
NO	0,15	0,51
H_2	12,36	6,26
N_2	23,5	25,7
CH_4	1,10	1,18
$HCN + C_2N_2 + NH_3$	1,40	5,42

The composition of the products of an explosion surrounded by inert material has been more specifically studied for charges of industrial explosives for underground workings (primarily ammonite).

As we noted above, explosives intended for blastings under the earth can be used in mines only when the quantity of poisonous gases formed during explosion does not exceed a certain limit. This limit was earlier (1935) determined, in the following way.

At that time explosives with a positive oxygen balance or an oxygen balance close to zero were studied by the method of explosion of freely suspended charges in an evacuated bomb. In these conditions the explosives form a small quantity of carbon monoxide and a very small quantity of nitrogen oxide, in all not more than 50 l for 1 kg of explosive. This number was taken as the norm.*

Subsequently, this norm was used not only to evaluate the suitability of newly developed explosives, but also in designing ventilation of mines, since it was not known that the composition of the products of explosion can depend greatly on the conditions in which the explosion occurs. When the quantity of poisonous gases, formed during blastings, was determined directly in the pits, it was discovered that in the shaft many times greater quantities of such gases, expecially nitrogen oxides, are obtained than in a bomb during an explosion of a freely suspended charge. Thus, 62% gelatin-dynamite, which formed only traces of nitrogen oxides in a bomb, in a mine gave off 5-l of these to 1 kg of explosive; still larger quantities of nitrogen oxides were formed during an explosion of ammonite No. 2 (12% trotyl and 88% ammonium nitrate).

Subsequent experiments, conducted at first in the Makeyevskiy Scientific Research Institute, mainly with ammonite, showed that large quantities of poisonous gases can be obtained also during an

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*We must note that this norm is rather strict. For comparison we may point out that in the United States, for instance, using this index, better safety explosives (so-called class 1) can form up to 78 l of poisonous gases per kilogram of explosive, second class explosives, also permitted in mines, can form up to 156 l of poisionous gases per 1 kg.

explosion in a bomb, if the charge is surrounded which is finely ground or easily crushed by an explosion by medium (quartz sand, coal, ores, and various minerals). These researches showed that despite the widely held opinion at that time, on a positive or zero oxygen balance of an explosive is not sufficient to keep the products of explosion from containing carbon monoxide.

The basic factor determining the quantity of nitrogen oxides and carbon monoxide formed during an explosion of ammonite, is their detonational ability. This ability is caused, on the one hand, by the composition: the more the ammonite contains of the most explosive component and the greater the detonational ability of that component, the less poisonous gases are formed, in otherwise equal conditions. On the other hand, the detonational ability is associated with the degree of milling and depends on the thoroughness of mixing of the components. The finer they are milled and the better they are mixed, the greater the detonational ability and the smaller is the amount of poisonous gases, which are formed.

Finally, as experiments have shown, it is possible to affect the formation of poisonous gases by introducing salts into the composition of the ammonite (for instance, KNO_3, KCl, NaCl, and so forth), which catalytically accelerate the interaction between the components of the explosives the intermediate products of their transformation.

All these patterns may be explained from the following data on the process of explosion of powder mixtures.

The propagation of a chemical reaction in this case takes place in a flow (penetration of the gasiform products of transformation into the gaps between the particles of the explosive) or in bubbles (compression of gaseous inclusions). Hot gases embrace and ignite the particles of the components of the explosive, causing their gasification.

The products of gasification themselves become involved in subsequent reactions. In the case of ammonites the intermediate products of these reactions are, in particular, nitrogen oxide and carbon monoxide. The smaller the particles, especially the particles of the most active component, the faster their combustion occurs. The combustion rate of particles also depends on the pressure at which it takes place. Along with this the heat of explosion, plays a role, determining the temperature of the gases in whose atmosphere the combustion of particles occurs. The catalysts accelerate the interaction among the intermediate products of transformation.

Table 7.4. The Effect of the Composition of Ammonite and the Degree of Milling of its Components n the Formation of Nitrogen Oxide and Carbon Monoxide During an Explosion of a Charge with a Liner of Quartz Sand

№ Experiment	Composition of ammonite in %				Oxygen balance %	Quantity of gases liter/kg		Note
	Trotyl	Ammonium nitrate	Wood flour	Potassium nitrate		$NO+NO_2$	CO	
1	12	88	—	—	+8,7	29	35	Quantity of sand 230 g
2	15	85	—	—	+5,9	19	35	
3	21,3	78,7	—	—	0	8	48	
4	25	75	—	—	—3,5	2,4	68	
5	12	84	4	—	+2,5	19	36	
6	15	81	4	—	—0,3	10	48	
7	12	73	—	15	+11,6	0,1	15	Quantity of sand 1000 g
8	12	73	—	15		27	6	Quantity of sand 200 g
9	15(№ 16)*	81(№ 16)	4(№ 16)	—	—0,3	10	48	Quantity of sand 230 g
10	15(№ 49)	81(№ 49)	4(№ 16)	—		0,15	40	
11	15(№ 73)	81(№ 73)	4(№ 16)	—		0	40	
12	15(№ 16)	81(№ 16)	4(№ 16)	—	—0,3	10	48	
13	15(№ 16)	81(№ 49)	4(№ 16)	—		7	42	
14	15(№ 49)	81(№ 16)	4(№ 16)	—		4	40	
15	15(№ 49)	81(№ 49)	4(№ 16)	—		0,15	40	

*The number of the sieve is shown in parentheses (number of holes per 1 cm), through which a given component is milled.

The totality of these effects determined the extent to which the products of explosion approach chemical equilibrium before contact with inert medium and cooling during expansion delay further development of reactions.

These considerations can be illustrated by the following experiment data from published works. In an example of two-component (trotyl-ammonium nitrate) and three-component (trotyl — wood flour — ammonium nitrate) ammonite the effect of the composition of the ammonite, the degree of crushing of the components, and the introduction of certain salts into the composition of the ammonite on the formation of nitrogen oxide and carbon monoxide during the explosion was studied. The results of these experiments are given in Table 7.4.

An increase in the content of trotyl, as the data in Table 7.4 show, greatly decreases the quantity of nitrogen oxide formed. Ammonite with 25% trotyl will form 10 times less nitrogen oxides during an explosion than ammonite with 12% trotyl. With an increase in the content of trotyl the quantity of carbon monoxide increases only 2 times. We should note that not only ammonite 75/25, with a negative oxygen balance, but also ammonite 88/12, containing a surplus of oxygen, forms carbon monoxide in the products of explosion. A decrease in the quantity of nitrogen oxides, formed during the explosion of ammonite 88/12 can be attained not only an increase in the content of trotyl, but also by the introduction of wood flour to replace part of the nitrate. The heat of explosion, and consequently the temperature of the gases increase. An increase in temperature accelerates combustion of the particles, and they succeed to a great degree in burning to the point of scattering. The content of nitrogen oxide in the products of explosion may be lowered also by the introduction of potassium nitrate and certain other salts into the composition of the ammonite. The action of these salts, is apparently determined by their catalytic effect on the combustion of scattering particles of the explosive. In spite of a certain decrease in the heat of explosion with the addition of potassium nitrate to ammonite with a positive oxygen balance, the completeness with which the reactions take place increases and the quantity of nitrogen oxide decreases. The effect of potassium nitrate appears, however, to depend in various degrees upon the quantity of inert material surrounding the charge (see Experiments 7 and 8 in Table 7.4).

The formation of nitrogen oxides is also greatly affected by the fineness to which the components are ground: this determines the total surface and combustion time. An increase in the fineness grinding trotyl and ammonium nitrate in triple ammonite (trotyl — nitrate — wood flour) leads to a sharp decrease in the amount of nitrogen oxide formed. Experiments, in which only one of the two basic components of the 3-part mixture was finely ground have shown that the milling of the trotyl has a greater effect on the formation of nitrogen oxide than the milling of the nitrate. Clearly the combustion of the trotyl, which have a high caloric (value and consequently the temperature of combustion), stimulates the combustion of ammonium nitrate particles more than the reverse.

The use of these laws in setting up the composition of ammonite in and the technology of their manufacture not only leads to a sharp decrease in the quantity of poisonous gases formed during blastings, but at the same time intensifies considerably the effect of explosion; because of an increase in the completeness with which reactions take place the effective heat of explosion is increased — this is the main factor determining efficiency.

§ 4. The Volume of the Products of Explosion

As we have noted, the gasiform products of explosion are the direct agents, by means of which the energy given off is turned into work. The knowledge of the volume and composition of the gasiform products of explosion allows us to calculate the maximum temperature which can be reached in the explosion.

If we know the equation for the chemical transformation in the explosion, then calculation of the volume V_0 of the products of explosion, formed per 1 kg of explosive under normal conditions is done by using Avogadro's hypothesis. Naturally we do not consider water, and, solid products as gases in this, since their volume is negligible compared to the volume of gases.

For instance, for ammatol 80/20 the equation of chemical transformation in an explosion is

$$11{,}35NH_4NO_3 + C_7H_5(NO_2)_3 = 7CO_2 + 25{,}2H_2O + \\ + 12{,}85N_2 + 0{,}425O_2$$

and

$$V_0 = \frac{(7 + 25{,}2 + 12{,}85 + 0{,}425)\,22{,}4 \cdot 1000}{227 + 11{,}35 \cdot 80} = 898 \text{ liter/kg.}$$

In parentheses we give the sum of the numbers of moles of gases, formed and in the denominator we give the weight of the substances on the left side of the equation, in grams.

In the common form for the equation of explosion,

$$m_1M_1 + m_2M_2 + \ldots + m_kM_k = n_1N_1 + n_2N_2 + \ldots + n_pN_p$$

the volume of gases V_0 may be expressed by the following formula

$$V_0 = \frac{(n_1 + n_2 + \ldots + n_p)\,22{,}4 \cdot 1000}{m_1M_1 + m_2M_2 + \ldots + m_kM_k}, \qquad (7.7)$$

where M_1, M_2 ... N_1, N_2 etc. are the molecular weights of the respective components of the explosive and explosion products, and m_1, m_2, n_1, n_2 etc. are the number of moles of the compounds entering into the composition of the explosive and the gasiform products of explosion.

Table 7.5. The Volume of Gasiform Products of Explosion of Certain Explosives According to (Apin and Belyayev)

Explosives	ρ g/cm^3	V_0 liter/kg	CO/CO_2
Trotyl	1.5 0.85	750 870	3.2 7.0
Hexogene	1.5 0.95	890 950	1.68 1.75
Trotyl/hexogene (50/50)	1.68 0.9	800 900	2.4 6.7
Picric acid	1.5 1.0	750 780	2.1 4.0
Tetryl	1.55 1.0	740 840	3.3 8.3
PETN	1.65 0.85	790 790	0.5-0.6
Nitroglycerine	1.6	690	–
Ammatol 80/20	1.3 0.9	890 880	– –
Mercury fulminate	3.77	300*	–

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*For mercury in a vapor state.

For an explosive whose products of explosion do not contain solid matter, the V_0 is in inverse proportion to the average molecular weight of the gases formed in the explosion. Therefore, the smaller the molecular weight of the gasiform products of explosion, the larger is the

V_0. The lightest of the gases formed in an explosion of organic explosive is hydrogen, and the heaviest is carbon anhydride. If the products of explosion consisted entirely of hydrogen, then V_0 would be equal to 11,130 l per kg; if they consisted only of carbon anhydride, then V_0 would be equal to 506 l per kg. A relatively large volume of gases is formed by explosives containing much hydrogen, even in the explosion it is oxidized to water. The formation in the explosion of solid products decreases V_0; therefore for an organic explosive with a strongly negative oxygen balance, a decrease in the density of the substance causes an increase in the volume of gasiform products of explosion at the expense of displacement of the reaction equilibrium

$$CO \rightleftarrows {}^1/_2 CO_2 + {}^1/_2 C$$

to the left, combined with an increase of volume.

In Table 7.5 we give the experimental data of Apin and Belyayev on the significance of the volume of gasiform products of explosion (gasiform water) for certain explosives, and also the CO/CO_2 ratio.

CHAPTER VIII

HEAT, TEMPERATURE AND PRESSURE OF EXPLOSION

Expanding gaseous products of an explosive transformation, heated to a high temperature as a result of the heat given off during this transformation, produce the mechanical work of the explosion. The magnitude of the heat of explosion (and also of the volume of the gases formed) permits an estimate of the potential efficiency (explosive effect, see p. 645) of the explosive. Knowledge of the heat of explosion, taking into account the density of the explosive and the speed of detonation permits us ultimately to judge the destructive effect of the explosion on the atmosphere in direct proximity to the charge (so-called brisance, see p. 658). For the quantitative characteristic of the throwing, splintering, thermal and other types of effects of products of explosive transformation it is necessary to know the heat of explosion, and the temperature and pressure of its products. These magnitudes, as we will see, are interrelated among themselves, and for calculating the latter two it is necessary to know the heat of explosion. We will begin the following presentation with the methods of determining the heat of explosion.

§1. Methods of Determining the Heat of Explosive Transformation

The quantity of heat given off during an explosive transformation (burning or detonation) of a defined mass of explosive is called the heat of explosion. In practice 1 kg is taken as the unit of mass during calculations of the heat of explosion.

For determination of the heat of explosion two methods, calculating and experimental, are used.

1. Calculation of the Heat of Explosion

The heat of explosion is calculated on the basis of the Hess law. This law, as is known, says that the thermal effect of the chemical transformation of a system depends only on its initial and final states, and does not depend on intermediate states, i.e., on the course of transition.

In application to the thermochemistry of explosives, we can write the Hess Law in the form of the relationship:

$$Q_{1-2}+Q_{2-3}=Q_{1-3}. \tag{8.1}$$

Indices 1, 2 and 3 designate correspondingly three states – initial (1), intermediate (2) and final (3); Q_{1-2} is the heat which is given off or absorbed during the transition from state 1 to state 2; Q_{2-3} – the heat of the transition from state 2 to state 3 and Q_{1-3} – the heat of the transition from state 1 directly to state 3.

Depending upon which thermochemical characteristics of the explosive (the heat of formation, the heat of combustion, the heat of explosive transformation, the thermal effect of the reaction of obtaining the explosive and others) are known, and which it is required to calculate, three basic variants of calculations are possible.

One of them is the calculation of the heat of explosion, where the heat of formation of the explosive and the equation of explosion serve as initial data.

For that case we will take the following designations in the equation (8.1):

State 1 — the elements in standard conditions.*

State 2 — the explosive under standard conditions.

State 3 — the products of the explosion under those same conditions.

Then Q_{1-2} — the heat of formation of the explosive from the elements,

Q_{2-3} — the heat of explosion,

Q_{1-3} — the heat of formation of the products of the explosion from the elements.

From the equation (8.1)

$$Q_{2-3}=Q_{1-3}-Q_{1-2}.$$

The heat of formation of the basic explosive compounds, the components of explosive mixtures and the products of the explosion are given in Table 8.1 and in more detail — in Appendix 5.

As an example we will calculate the heat of explcsion of ammatol 80/20, the equation of explosion of which has the form:

$$11,35NH_4NO_3+C_7H_5(NO_2)_3=7CO_2+25,2H_2O+12,85N_2+0,125O_2.$$

The heat of formation from the elements of the substances, standing in left part of the equation (see Table 8.1), is

$$Q_{1-2}=11,35\cdot 87,36+17,5=1009,04\ \text{kcal},$$

where 87.36 kilocalorie/molecule — heat of formation of ammonium nitrate,

17.5 kilocalorie/molecule — heat of formation of trotyl.

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*Different authors consider different conditions as standard for calculating thermochemical magnitudes. Standard pressure is usually 1 atm(abs), and standard temperature accepted as 0°, 18° (as accepted in this book) or 25°C. The heat of formation of elements in standard conditions is assumed equal to zero.

Table 8.1. The Heats of Formation of Certain Explosives and Products of Explosion.

Substance	Heat of formation in kilocalorie/molecule at 18°C and constant pressure	Substance	Heat of formation in kilocalorie/molecule at 18°C and constant pressure
Trinitrotoluene	17.5	Cellulose	230.3
Nitrocellulose (1200% N)*	683.3	Water (gas)	57.78
Nitroglycerine	98.63	Water (liquid)	68.37
Drglycoldinitrate	104.2	Carbon dioxide	94.51
PETN	129.37	Carbon monoxide	26.88
Hexogene	-15.64	Nitrogen oxide	-21.6
Dinitronapthalene (1.5)	-3.6	Methane	18.3
Ammonium nitrate	87.36	Aluminium oxide	399

*In kilocalorie/kilogram.

The heat of formation of products of explosion from elements

$$Q_{1-3} = 7 \cdot 94.51 + 25.2 \cdot 57.78 = 2117.64 \text{ kcal},$$

where 94.51 and 57.78 are correspondingly the heats of formation of 1 gram/molecule of carbonic acid and gaseous water from the elements;

$$Q_{2-3} = Q_{1-3} - Q_{1-2} = 2117.64 - 1009.04 = 1108.60 \text{ kcal}.$$

The magnitude obtained represents the heat of explosion at constant pressure, i.e., with such a volume of gaseous products of explosion, which they occupy under standard conditions (18°C and 760 mm Hg). This magnitude is designated Q_p. If the reaction of an explosive transformation actually takes place, for instance, during detonation, and is completed so that its products are essentially expanded, then it is considered that the reaction occurs without a change of volume i.e., the products of the explosion occupy, upon completion of the reaction, that volume which the initial explosive occupied. The heat of reaction with constant volume is designated

Q_v. It is not difficult to see that $Q_p < Q_v$, since in the latter case a part of the energy is not expended on the work of the expansion of gases from the volume of the explosive to the volume corresponding to atmospheric pressure and the given temperature (18°C), i.e., to 23.9 liters for every gram/molecule of gases.

In order to change from the heat of explosion at constant pressure to the heat of explosion at constant volume, we have to add to Q_p the magnitude $q = 0.58N$, where N is the number of moles of gaseous products of explosion (water is taken for the gas). The factor 0.58 represents the work, expressed in kilocalories, of the expansion at constant pressure, equal to 1 atm(tech.), of one mole of gases from the initial volume (assumed equal to zero) to the volume occupied by the gas at 18°C and pressure of 760 mm Hg.*

In our example

$$q = 0.58\ (7 + 25.2 + 12.85 + 0.425) = 26.38 \text{ kcal.}$$

Correspondingly

$$Q_v = Q_p + q = 1108.60 + 26.38 = 1134.98 \text{ kcal.}$$

The derived heat of explosion pertains to the quantity of the mixture, expressed by the equation which is written above. The heat of explosion for 1 kg of explosive at constant volume is

$$Q_v = \frac{1134.98 \cdot 1000}{11.35 \cdot 80 + 227} \approx 1000 \text{ kcal/kg.}$$

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*$q = p_0 v_t \frac{1}{E} N$, where p_0 is the pressure in kilograms per square meter, v_t is volume of 1 mole of gases at temperature t°C in cubic meters, and $1/E = 1/427$ is the mechanical equivalent of heat

$$q = \frac{10\,333 \cdot 0{,}02241 \cdot 291}{273 \cdot 427} N = 0{,}58N \text{ kcal.}$$

In the case of explosive mixtures with a positive or weakly negative oxygen balance, during the explosion of which elemental carbon is not given off, an approximate calculation of the heat of explosion can be made according to the heats of combustion* of the organic components and the heats of transformation to the final products, formed during explosion, of the mineral salts which comprise the explosive. Thus, for instance, for nitroglycerine, trotyl, ammonium nitrate, sodium nitrate and cellulose the equations of complete combustion or transformation can be written according to the following example:

$$C_3H_5(NO_3)_3 = 3CO_2 + 2\frac{1}{2}H_2O + 1\frac{1}{2}N_2 + \frac{1}{4}O_2;$$

$$C_7H_5(NO_2)_3 + 5\frac{1}{2}O_2 = 7CO_2 + 2\frac{1}{2}H_2O + 1\frac{1}{2}N_2;$$

$$NH_4NO_3 = N_2 + 2H_2O + \frac{1}{2}O_2;$$

$$2NaNO_3 + CO_2 = N_2 + Na_2CO_3 + \frac{3}{2}O_2;$$

$$C_6H_{10}O_5 + 6O_2 = 6CO_2 + 5H_2O.$$

For each of these equations it is easy to calculate the quantity of heat released or absorbed, and also the number of moles of each of the products of the reaction per kilogram of the compound. Thermal effect is computed at constant volume, considering that water will be formed in the liquid state. Oxygen or carbonic acid, necessary for completion of the reaction of oxidizing fuel or transforming the nitrate of a metal to the carbonate, naturally, are expressed by negative values. They permit us to calculate for the mixture the heat of explosion and the composition of its products by simple addition:

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*Let us remember that the quantity of thermal energy, released during the reaction of the combustion of a unit of mass of a substance in oxygen, with the formation of products of complete oxidation (CO_2, H_2O, and so on), is called the heat of combustion.

$$Q = \sum_r w_r Q_r; \qquad (8.2)$$

$$P_N = \sum_r w_r P_r, \qquad (8.2a)$$

where w_r – percentage composition (by weight) of component r in the composition of the explosive, Q_r and P_r – constants for that component, and P_N – content of substance N in the products of explosion. Values of magnitudes Q_r and P_r are given for typical components of industrial explosives in Table 8.2.

Table 8.2. Heat and Composition of Products of the Complete Combustion or Decomposition of Certain Components of Explosive Mixtures

Substance or reaction	Heat of complete combustion Q_r kilocalorie per kilogram (H_2O liquid, v = constant)	P_r for products in moles/kg				
		CO_2	H_2O	N_2	O_2	Other substances
a. Inorganic oxidizers						
Nitrate of ammonium	628	—	25.0	12.5	6.25	—
Barium nitrate (higher than 1300°C)	-389	—	—	3.82	9.56	3.82BaO
Barium nitrate (lower than 900°C)	-151	-3.82	—	3.82	9.56	3.82$BaCO_3$
Potassium perchlorate	+13	—	—	—	14.43	7.21KCl
Potassium nitrate	-268	-4.94	—	4.94	12.36	4.94K_2CO_3
Sodium nitrate	-267	-5.88	—	5.88	14.7	5.88Na_2CO_3
b. Organic compounds						
Cellulose	4185	37.0	30.9	—	-37.0	
2.4-Dinitrotoluene	4660	38.5	16.5	5.5	-35.7	
Manila paper	4254	30.1	33.4	—	-32.3	SiO_2 1.8
Mononitrotoluene (meta)	6490	51.1	25.6	3.7	-56.6	
Nitrocellulose (12% N)	2477	22.8	14.7	4.3	-12.1	
Nitroglycerine	1623	13.2	11.0	6.6	+1.1	
Nitroglycol	1764	13.2	13.2	6.6	—	
Paraffin	11120	70.5	74.1	—	-107.5	
Trotyl	3596	30.8	11.0	6.6	-23.1	
Sawdust	4762.	39.7	35.4	—	-43.2	

Table 8.2. Continued

Substance or reaction	Heat of complete combustion Q_r kilocalorie per kilogram (H_2O liquid, v = constant)	P_r for products in moles/kg				
		CO_2	H_2O	N_2	O_2	Other substances
	c. Other components					
$2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2$	−117	5,95	5.95	—	—	5,95Na_2CO_3
$BaCO_3 \rightarrow BaO + CO_2$	−321	5,07	—	—	—	5,07BaO
$CaCO_3 \rightarrow CaO + CO_2$	−420	10,0	—	—	—	10,0CaO
$Na_2B_4O_7 \cdot 10H_2O \rightarrow Na_2B_4O_7 + 10H_2O$	−94	—	26,2	—	—	2,62 $Na_2B_4O_7$
$4Al + 3O_2 \rightarrow 2Al_2O_3$	7382	—	—	—	−27,8	18,5Al_2O_3

For an explosive with a zero or positive oxygen balance the result obtained the heat of complete combustion – is directly equal to the heat of explosion. For an explosive with a negative oxygen balance it is necessary to introduce a correction for the incomplete combustion organic substances into the result obtained. The heats of oxidation of carbon monoxide to carbonic acid and hydrogen to water (liquid) at constant volume and $0^\circ C$ are approximately equal (corresponding to 67.3 and 67.5 kilocalories). Therefore, for each mole of deficient oxygen the heat of explosion is rendered roughly 135 kilocalories less than the heat of complete combustion. For explosives with a negative oxygen balance

$$Q_{v(H_2O_{ж})} = \sum w_r Q_r + \frac{135 \cdot 1000}{100 \cdot 32} a \doteq \sum w_r Q_r + 42,2a, \qquad (8.26)$$

[ж = liq = liquid]

where a is the oxygen balance in grams per 100 grams of explosive.

The method presented permits us to obtain in good approximation the heat of explosion by the simplest means. In this connection the heat of reaction with formation of water, as a liquid, is also calculated $Q_{v(H_2O_{liq})}$. In reality water, at the moment of explosion will be, naturally, in the gaseous state. The value of the heat of explosion with the formation of gaseous water $Q_{v(H_2O_g)}$ is obtained by subtracting the heat of evaporation of water from $Q_{v(H_2O_{liq})}$:

$$Q_{v(H_2O_г)} = Q_{v(H_2O_ж)} - 10{,}01n, \qquad [г = g = gas] \qquad (8.3)$$

where n is the number of moles of water formed.

We will conduct by the method examined the calculation for ammatol 80/20. The heat of complete combustion of ammonium nitrate and trotyl in kilocalories per kilogram at constant volume and water as a liquid are respectively 628 and 3596 kilocalories per kilogram. The heat of explosion for 1 kg of ammatol

$$Q_{v(H_2O_ж)} = \frac{80 \cdot 628}{100} + \frac{20}{100} 3596 = 1222 \text{ kcal/kg.}$$

The number of moles of water for 1 kg of explosive according to Table 8.2 equals

$$n = \frac{80 \cdot 25}{100} + \frac{20 \cdot 11}{100} = 20 + 2{,}2 = 22{,}2.$$

After the substitution

$$Q_{v(H_2O_г)} = 1222 - 10{,}01 \cdot 22{,}2 = 1000 \text{ kcal/kg.}$$

2. Calculation of Heat of Combustion of Smokeless Powders

On the same principle — the additivity of heats of chemical transformation — is based the method of calculating the heat of burning nitroglycerine smokeless powders, widely applied in powder-making. The calculation originates from the assumption that the heat of burning of powder can be expressed as the sum of the products of the contents of the individual components in the powder for thermochemical constants, characterizing each of these components,

$$Q_ж = m_1\beta_1 + m_2\beta_2 + \ldots + m_n\beta_n = \sum_1^n m\beta. \qquad (8.4)$$

In expression (8.4) Q_{liq} is the heat of combustion of powder in kilcal/kg. At constant volume and water as a liquid m_1, m_2 etc. – contents of components in % and β_1, β_2 etc. – their thermochemical constants.

The assumption of the additivity of heats of combustion is accurate upon two conditions:

1) if the composition of the products of combustion is determined only be the equilibrium of the reaction of water as a gas, i.e., the products of burning do not contain free oxygen or carbon,

2) if heat of combustion of powder is calculated with water as a liquid.

The thermal effect of the formation of one mole of water according to the reaction of water as a gas is negative, according to the absolute value almost exactly equal to the heat of condensation of one mole of steam. Therefore, the change of the thermal effect upon the displacement of equilibrium on this or that side is compensated by the change of the total heat of condensation of steam, the number of moles of which changes correspondingly. In other words, the thermal effect of the combustion of powder, calculated for water as a liquid, is a constant magnitude, not depending on temperature attained during combustion.

At fulfillment of above-indicated conditions the thermochemical constant of each of the components of the powder can be calculated as the heat of its transformation to CO, H_2O, H_2 and CO_2. If a component contains a surplus of oxygen, then the necessary carbon and hydrogen are drawn from other components, where the interaction of oxygen with them yields a corresponding quantity of heat. If a component contains a surplus of carbon, then the quantity of oxygen necessary for its oxidation is borrowed from the carbon dioxide, obtained during the combustion of other components. The transformation of carbon, as a result of the oxygen of carbon dioxide, to carbon monoxide is accompanied by a corresponding absorption of heat.

Thus, for calculating β we obtain the following expression,

$$\beta = 0{,}01\,\frac{(94{,}51\,[CO_2] + 26{,}88\,[CO] + 68{,}37\,[H_2O] - Q_{\text{обр}}}{M} + \\ + \frac{135{,}26\,[O_2] - 40{,}75\,[C] + 0{,}58n)\,1000}{M}, \tag{8.5}$$

[обр = hf = heat of formation]

where $[CO_2]$, $[CO]$, $[H_2O]$, $[O_2]$, $[C]$ are quantities of moles of corresponding products, formed during the combustion of one mole of a given substance as a result of its own oxygen;

Q_{hf} – the heat of formation of the substance in kilocal/mole with constant pressure and water as a liquid;

M – molecular weight of substance;

135.26 – heat of transformation of a mole of oxygen to CO_2 as a result of the oxidation CO (and approximately of hydrogen also);

40.75 – heat of oxidation of one gram-atom of carbon to CO as a result of the oxygen of CO_2;

94.51, 26.88 and 68.37 – heats of formation at constant pressure of CO_2, CO and H_2O respectively;

n – the number of moles of gases (without water and without oxygen), formed by a substance upon the decomposition and subsequent interaction of carbon with CO_2; the product 0.58n represents the difference between the heat of transformation at constant pressure and constant volume;

the factor 0.01 means that the calculation is conducted for 0.01 kg of a substance, i.e., for 1% with respect to 1 kg.

As an example we will calculate β for nitroglycerine and centralite.

The reaction of the decomposition of nitroglycerine

$$C_3H_5N_3O_9 = 3CO_2 + 2.5H_2O + 1.5N_2 + 0.25O_2.$$

According to the expression (8.5) we have:

$$\beta = 0{,}01\,\frac{(94{,}51\cdot 3 + 68{,}37\cdot 2{,}5 - 88{,}63 + 135{,}26\cdot 0{,}25 + 0{,}58\cdot 1{,}5)\cdot 1000}{227{,}09} = 17{,}7.$$

The reaction of the decomposition of centralite

$$C_{17}H_{20}N_2O = CO + 10H_2 + N_2 + 16C;$$

$$\beta = 0{,}01\,\frac{(26{,}88\cdot 1 - 31{,}9 - 40{,}75\cdot 16 + 0{,}58\cdot 28)\,1000}{268{,}35} = -23{,}9.$$

Application of the described method of calculation showed that the computed values of β do not always give the correct magnitude of the heat of combustion of powder, corresponding to the results of the experimental determination. This is explained by the fact that the calculation of β is conducted for chemically pure substances, whereas in technology products are used which contain a certain amount of impurities. Therefore, during the calculation of heat of combustion of powder it is preferred to use values of β determined experimentally for industrial products. Values of β obtained in this manner for a number of substances are given in Table 8.3.

As an example we will calculate the heat of combustion of powder. The calculation will be formulated in a small table, in the first column of which is given the composition of the powder (in % for the dry substance), in the second – the value of β for the components according to Table 8.3 and in the third – the product of the corresponding magnitudes from the first two columns

Nitrocellulose (N = 12.08%)	56	+9.0	+504
Nitroglycerine	36	+17.5	+630
Diamyl Phthalate	5	-19.5	-97.5
Centralite No. 1	2	-23.7	-47.4
Vaseline	0.7	-31.9	-22.3
Graphite	0.3	-30.0	-9
			958 kcal/kg.

Table 8.3. Values of the Thermochemical Constant β

Substance	$\beta_{experimental}$
Nitroglycerine	+17.5
Dinitrodiglycol	+10.5
Nitrocellulose containing N% of nitrogen	1.3N -6.7
Nitroguanidine	+6.6
Dinitrotoluene, pure	-1.1
Dinitrotoluene, technical	0.0
Dinitroxylene (N ≈ 13.5%)	-2.5
(N ≈ 12.5%)	-3.5
Dinitroanisole	+0.5
Dinitrophenetole	-1.0
Trinitrotoluene	+5.5
Dinitrodimethyl oxamide	+8.7
Centralite No. 1 (ethyl)	-23.7
Centralite No. 2 (methyl)	-22.9
Diphenylcarbanide	-20.5
Diphenylamine	-29.0
Diethyl phthalate	-16.0
Dilutyl phthalate	-20.0
Dianyl phthalate	-19.5
Alcohol, ethyl	-17.5
Acetone	-20.5
Camphor	-28.0
Vaseline	-31.9
Graphite	-30.0
Water	0

If the powder contains 0.5% moisture (above 100%), then, considering that β water is equal to 0, we finally obtain

$$Q_{ж} = \frac{958}{1{,}005} = 953 \text{ kcal/kg.}$$

The calculation of the heat of combustion according to the values of β originates from the assumption that chemical reactions during combustion proceed to equilibrium. In this case the possibility of the dissociation of carbon dioxide and steam into free oxygen, hydroxyl and atomic hydrogen, and also the possibility of the formation of nitrogen oxide is not considered. The factors not considered in the calculation obtain a greater value, the higher the heat of combustion of the powder and the lower the pressure, under which it proceeds. Therefore, under conditions of a gun barrel firing their value is small; but during a rocket firing the value may be substantial.

3. Calculation of the Heat of Formation of an Explosive

If the heat of explosion and the composition of the products of an explosion are known from an experiment, then it is possible to calculate the heat of formation of an explosive according to the following example.

Preserving the designations, accepted in the first variant of the calculation (p. 596), we obtain according to the law of Hess

$$Q_{1-2} = Q_{1-3} - Q_{2-3}.$$

As an example we will calculate the heat of formation of PETN. The heat of explosion of PETN is equal (at constant volume, and water as a liquid) to 1373.3 kilocal/kg; the equation of explosion for 1 kg of explosive has the following form:

$$3{,}162C(CH_2ONO_2)_4 = 9{,}18CO_2 + 6{,}64CO + 10{,}97H_2O +$$
$$+ 1{,}69H_2 + 1{,}3NO + 0{,}36O_2 + 5{,}67N_2;$$
$$Q_{1-3} = 9{,}18 \cdot 94{,}51 + 6{,}64 \cdot 27{,}17 + 10{,}97 \cdot 67{,}50 + 1{,}3(-21{,}6) =$$
$$= 1760{,}4 \text{ kcal.}$$

The heat of formation of 1 kg of PETN at constant volume

$$Q_{1-2} = 1760.4 - 1373.3 = 387.1 \text{ kcal.}$$

Correspondingly for 1 mole of PETN the heat of formation is equal to

$$\frac{387.1}{3.162} = 122.4 \text{ kcal.}$$

The heat of formation at constant pressure

$$Q_p = 122.4 + 0.58 \cdot 12 = 129.4 \text{ kcal},$$

where 12 — number of moles of gaseous elements, necessary for the formation of 1 mole of PETN.

In many cases the calculation of the heat of formation of explosives can be simplified, if, instead of the reaction of explosion, the reaction of complete combustion is used. In this case the number of compounds comprising the products of transformation being significantly less the quantitative analysis of the latter is simplified, and the equation of transformation based on its results is, therefore, made more reliable.

For the calculations we take the following designations:

State 1 — elements.

State 2 — explosive + oxygen.

State 3 — products of complete combustion.

Q_{1-2}, Q_{2-3} and Q_{1-3} — respectively the heats of formation of explosives, of its combustion, and the formation of the products of combustion from the elements. According to the law of Hess the heat of formation

$$Q_{1-2} = Q_{1-3} - Q_{2-3}.$$

In the form of an example we will calculate the heat of formation of trotyl, the equation of combustion of which has the following form:

$$C_7H_5(NO_2)_3 + 5.25O_2 = 7CO_2 + 2.5H_2O + 1.5N_2 + 816.8 \text{ kcal}$$

(at constant volume, water as a liquid);

$$Q_{1-2} = 7 \cdot 94.51 + 2.5 \cdot 67.50 - 816.8 = 13.5 \text{ kcal/mole.}$$

The heats of combustion of a number of explosives are given in Appendix 6.

For nitro-compounds, the heat of combustion of which is not experimentally determined, it can be calculated approximately by the method of Young, Keyes and others. They established that molar heat of combustion to carbon dioxide, water as a liquid, and nitrogen is linearly bound with the number of atoms of oxygen s, necessary for combustion (Fig. 8.1). This is accurate for alkanes (Q_v = 52.48s + 6, straight line A) for normal monoolefins (Q_v = 52.48s + 20, straight line Б) for acetylene hydrocarbons (Q_v = 52.48s + 43.3, straight line B), for amines (Q_v = 51.8s, straight line Г) and for compounds of the benzene series (Q_v = 52.4s, straight line Д). An analogous relationship is accurate also for nitro-compounds, if during the calculation the oxygen bound with the nitrogen in the nitro groups is not taken in consideration. In this case Q_v = 50.3s, straight line E.

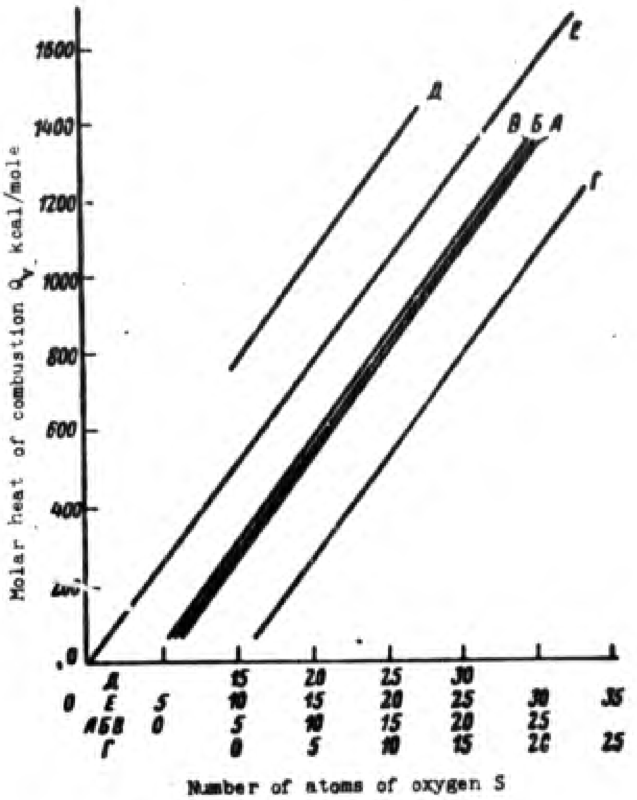

Fig. 8.1. Dependence of the molar heat of combustion of alkanes (A), olefins (Б), compounds of the benzene series (Д), acetylene hydrocarbons (B), amines (Г) and nitro compounds (E), on the number of atoms of oxygen necessary for combustion.

This simple method gives a good conformity between the experimental and calculated data for normal nitro alkanes and nitro compounds of the aromatic series. For compounds of more complicated structure, for instance cyclotrimethylene trinitramine and N-Nitrosuccinimide, large divergences are observed. In exactly the same way the comparison of data for compounds with a different position of the substitute shows that orthoderivatives have a larger heat of combustion than meta-derivatives, and the latter ones larger than steam, if only the compound is not able to be stabilized by means of the formation of a hydrogen bond.

As example we will calculate the heat of combustion of 2-4-6-trinitrophenol. The number of atoms of oxygen necessary for combustion $s = 12.5$; $Q_v = 50.3 \cdot 12.5 = 628.8$ kilocal/mole; experimentally determined $Q_v = 621.1$ kilocal/mole.

4. Calculation of the Heat of Reaction of the Production of an Explosive

Besides the heat of formation of an explosive and the heat of explosion, the thermal effect of the reaction of the production of explosive from initial products has important significance for industry. Knowledge of this magnitude is necessary during the thermal calculations of apparatuses. It may be calculated, if the heats of formation from the elements of the explosive, of the products of reaction associated with the explosive, and of the initial substances are known.

We will take the following designations:

State 1 — elements.

State 2 — the initial substances, entering into the reaction.

State 3 — explosives and other products, formed during the reaction.

Q_{1-2} with these designations will be heat of formation of the initial substances from the elements, Q_{1-3} — the heat of formation of explosives and other products of the reaction from the elements,

Q_{2-3} — the thermal effect of the reaction of the production of explosives. According to the law of Hess

$$Q_{2-3} = Q_{1-3} - Q_{1-2}.$$

As example we will examine the reaction the nitration of glycerine, expressed by the equation

$$C_3H_5(OH)_3 + 3HNO_3 = C_3H_5(ONO_2)_3 + 3H_2O + Q_{2-3}.$$

Q_{1-2} is equal to the sum of the heats of formation of 1 mole of glycerine and 3 moles of nitric acid

$$Q_{1-2} = 1 \cdot 161.2 + 3 \cdot 41.66 = 286.18 \text{ kcal.}$$

Q_{1-3} is equal to the sum of the heats of formation of 1 mole of nitroglycerine and 3 moles of water (liquid)

$$Q_{1-3} = 1 \cdot 88.63 + 3 \cdot 68.37 = 293.74 \text{ kcal.}$$

The heat of reaction $Q_{2-3} = 293.74 - 286.18 \approx 7.6$ kilocal for 1 mole of glycerine. During practical calculations one should not forget that the water released hydrates the acids of the nitrating mixture with significant thermal effect, which plays a fundamental role in the heat balance of the process.

5. The Experimental Determination of the Heat of Explosion

The heat of explosion can be determined by experimental means analogous to the determination of the efficiency of fuels in the Berthelot-Maler calorimetric bomb. In this case the bomb is filled not by oxygen, as usual, but with nitrogen or the air is pumped out and an explosion produced in a vacuum. An increase in the temperature of the water in the calorimeter, multiplied by the heat capacity of system — bonb + water + calorimetric vessel, gives the quantity of heat, released during the explosion.

In the Berthelot-Maler bomb, for secondary and launching explosives one can determine only the heat of combustion; it is possible to determine the heat of explosion in this bomb only for those substances which explode from incandescent wire, i.e., practically only for priming explosives and black powder. The use of a capsule-detonator for the excitation of explosion of substances which do not detonate from simple heating is impossible, in view of the comparatively small volume of the bomb and its low stability, which does not permit the use of large charges.

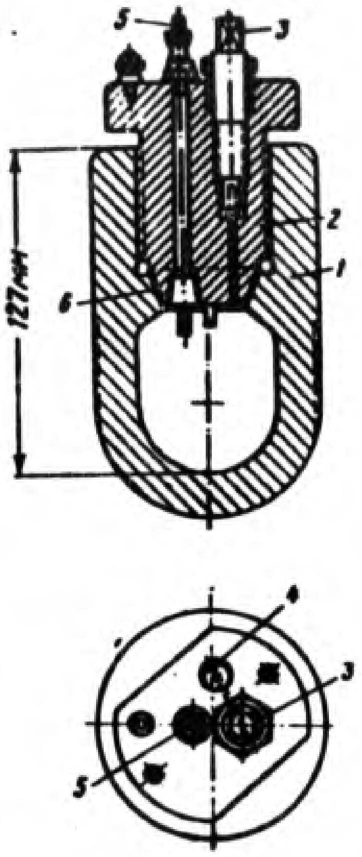

Fig. 8.2. Bomb for determination of the heat of explosion of explosives. 1 – body of bomb, 2 – bushing, 3 – valve, 4 – aperture for release of gases, 5 – electroinsulated inlet, 6 – copper packing cone.

For the direct determination of heat of explosion bombs of large dimensions and stability have been designed, allowing the detonation of significant charges by means of a capsule-detonator or other means. One such design is a calorimetric bomb, used in English laboratories (Fig. 8.2). The capacity of the bomb (124 cm^3) and its great durability permit the explosion in it of charge of explosives up to 12.4 grams. Triggering can be produced by the explosion of an electrolytic detonating gas under a pressure of 2 atm (tech.), ignited in its turn by an incandescent wire. The bomb is placed in the calorimeter and the increase of termperature determined. After the experiment, the volume and composition of the products of explosion are determined as well.

Apin and Belyayev used for determining the heat of explosion a thick-walled bomb (Fig. 8.3) of even greater volume (4.75 liters). It is possible to detonate in it charges of considerable weight (up to 50-100 grams) and it has, besides, a durable shell so that test conditions approximate the conditions in practice. Another distinction of the method developed for determining the heat of explosion lies in the rejection of a liquid calorimeter; the bomb itself serves this purpose, where the temperature is measured by three thermometers, the location of which can be seen in Fig. 8.3. The bomb is calibrated like a calorimeter – by burning in it a determined weight of benzoic acid in an atmosphere of oxygen. In thirty minutes, after burning the thermal effect, calculated by the increase of temperature of the bomb, constituted, due to heat loss, an average of 94% of the heat of combustion. On this base, during the experiments with explosives, we assumed that increase of enthalpy of the bomb constitutes also 94% of the heat of explosion. The authors estimate that the general error of calculation is 1-2%.

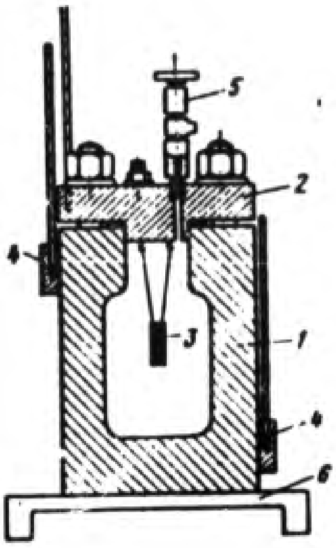

Fig. 8.3. Bomb of Apin and Belyayev for the determination of the heat of explosion of explosives. 1 – body of bomb, 2 – cover, 3 – charge, 4 – holders for thermometers, 5 – valve for evacuation and the release of gases, 6 – wooden support.

The values of heat of the explosion of a number of explosives, obtained by such method upon the explosions of charges through 50 grams in a lead casing 0.5 kg in weight, are given in Table 8.4.

Table 8.4. Heat of Explosion of Certain Explosives (According to Apin and Belyayev)

Explosive	Density ρ (grams/cm^3)	Heat of explosion $Q_v(H_2O_{gas})$ kcal/kg
Trotyl	1,5	1010
"	0,85	810
Hexogene	1,5	1290
"	0,95	1270
TH 50/50 (poured trotyl-hexogene)	1,68	1140
The same	0,9	1030
Picric acid	1,5	980
The same	1,0	910
Tetryl	1,55	1090
The same	1,0	920
PETN	1,65	1360
The same	0,85	1360
Nitroglycerine	1,6	1480
Tetranitromethane-benzene (87.5/12.5)	1,48	1650
Ammatol 80/20 (80% ammonium nitrate, 20% trotyl)	1,3	990
The same	0,9	960
Ammatol 40/60	1,55	1000
Mercury fulminate	3,77	410*
The same	1,25	380*

*For mercury in the vaporous state.

The calorimetric bomb, designed by Bikhel, has still a larger volume, 26 liters. It is possible to produce into by means of a capsule-detonator the detonation of explosive charges of considerable diameter weighing up to 100 grams; this to the greatest degree approximates the conditions of explosion found in practice, especially if the explosive is placed in a durable casing which slows down the dispersal of the products. Air is evacuated from the bomb before the experiment; it may also be filled with inert gas. In other respects the device differs from the usual calorimeter only in its large dimensions. The method of determination also has no principal differences.

During the determination of heats of explosion, obtained in the calorimetric bombs, it is necessary to bear in mind that the equation of explosion, and consequently also the thermal effect, can to a great extent depend on the conditions, in which the explosion takes place. Data obtained for a freely suspended charge in a calorimeter, have only conditional value, just as data obtained during explosion in a casing, if "hardening" of the composition of products is not provided.

Analogous complications arise during determination of the heat of combustion of powders in a calorimetric bomb. Even in the simplest case, when the composition of the products of combustion is determined only by equilibrium of the reaction of water vapor, upon cooling of the gases their composition changes. "Hardening" of equilibrium depends on the speed of cooling, but the latter is determined by a series factors – temperature, magnitude of internal surface and material of bomb, speed and temperature of combustion of the powder, density of loading and others. The temperature of "hardening" of equilibrium can be judged by the composition of the gases. During research in ordinary conditions this temperature is between 1500 and 1650°C. Inasmuch as displacement of equilibrium during cooling proceeds with the liberation of heat, then the thermal effect, calculated by reaction with the formation of water vapor, depends upon at what temperature the "hardening" of equilibrium has set in.

If one were to calculate the heat of combustion with water as a liquid (as it is determined during the experiment), then, as was explained above (see p.602), its magnitude does not depend on at what temperature the "hardening" of equilibrium of the reaction of water vapor occurred. Namely for this reason the heat of combustion with water vapor $Q_{vH_2O_{liq}}$ is usually used in powder-making for determining characteristics of powder.

§ 2. Burning and Explosion Temperatures

The products from the heat which is given off during the process of burning or explosion can be heated to a certain temperature. This temperature is called the burning (explosion) temperature.

A knowledge of the temperature of the burning of powders is essential for calculating the pressure which is built up in a barrel or rocket chamber during firing, for an estimate of the possibility of the formation of muzzle flame, and a characterization of the erosional capacity of powder gases. The explosion temperature is one of the basic parameters determining the danger of the application of explosives in coal mines in the presence of methane air or dust-air explosive mixtures. Finally, at least in the case of gas mixtures, a knowledge of the temperature of explosion and the composition of its gaseous products enables us to calculate the speed of detonation.

For a determination of the explosion temperature it is possible in principle to use both the experimental and also the calculating method. The experimental determination of the explosion temperature, however, is greatly hampered by two circumstances: large absolute values of temperature (to 5000°C) and its extraordinary brevity. The first condition impedes the selection of material for the measuring instrument all the more since a high temperature will be accompanied during the blast of condensed explosives by extremely high pressure which is, moreover, active in the form of a shock. By virtue of the brevity of the existence of the maximum explosion temperature, the usual instruments are inapplicable for its measurement inasmuch as they possess appreciable thermal inertia. Therefore, the basic method of determining the temperature of explosion at the present time is the computation method.

1. Computation of the Temperature of Explosion

Various formulas have been applied in computing the explosion temperature. Thus, in 1857 Bunsen and Shishkov used the formula

$$t = \frac{Q}{c},$$

for calculating the explosion temperature of black powder, where Q is the explosion heat, and c is the heat capacity of the products of the explosion which these authors considered constant. Later when it became clear that the heat capacity cannot be considered independently from temperature, Mallard and Le Chatelier adopted for temperatures higher than 1000°C a linear dependence of the heat capacity upon the temperature

$$c = a + bt,$$

where c is the mean heat capacity in an interval of temperatures from 0° to $t^{\circ}C$ and a and b are coefficients which are different for various gases.

Subsequently, as the experimentation and computation methodology was improved, the values of the heat capacities and their dependence upon temperatures were repeatedly revised and made more accurate. A summary of the values of heat capacity was published by Lewis and Elbe in 1951. We shall use these data (see Appendix 8 and 8a) also for our computations.

Inasmuch as the table of Lewis and Elbe does not show heat capacity directly, but the changes of the internal energy of gases in a definite interval of temperatures, it is expedient to conduct the calculation of the explosion temperature in the following manner.

We set for ourselves a certain value of the explosion temperature and calculate the change of the internal energy of all the explosion products during their heating from an initial temperature (291°K) to the temperature of explosion which we set. If the sum which is derived coincides with the explosion heat, then the temperature for which the calculation was made corresponds to the temperature of explosion. If this is not the case, then the computation is repeated while setting up accordingly in conformity with the modified value of the temperature.

Let us clarify what has been said in an example. The equation of the explosion of ammotol 80/20 has, as was noted above the following form:

$$11.35NH_4NO_3 + C_7H_5(NO_2)_3 = 7CO_2 + 25.2H_2O + \\ + 12.85N_2 + 0.425O_2 + 1135 \text{ kcal}.$$

We set as the temperature of explosion 3200°K (2927°C). The change of the internal energy ΔE for the products of explosion from 291 to 3200°K is:

$$\begin{aligned} CO_2 &= 33{,}998 \cdot 7 &&= 237{,}99 \\ H_2O &= 26{,}655 \cdot 25{,}2 &&= 671{,}70 \\ N_2 &= 18{,}217 \cdot 12{,}85 &&= 234{,}09 \\ O_2 &= 19{,}632 \cdot 0{,}425 &&= 8{,}34 \\ &&& \overline{1152{,}1.} \end{aligned}$$

Inasmuch as value ΔE was greater than the heat of explosion, it is necessary to set a smaller one which more closely approximates at a temperature of (3000°K). The change of the internal energy from 291° to this temperature constitutes

$$\begin{aligned} CO_2 &= 31{,}382 \cdot 7 &&= 219{,}67 \\ H_2O &= 24{,}466 \cdot 25{,}2 &&= 616{,}54 \\ N_2 &= 16{,}839 \cdot 12{,}85 &&= 216{,}38 \\ O_2 &= 18{,}112 \cdot 0{,}425 &&= 7{,}70 \\ &&& \overline{1060{,}3.} \end{aligned}$$

The change of internal energy during a change of temperature at 200° is 1152.1-1060.3 = 91.8 kilocalories. The difference of internal energy ΔE at 3200°K and of the blast heat constitutes 1152-1135 = 17

Kilcalories. While calculating approximately that during small changes of temperature ΔE is directly proportional to ΔT, we will find that this difference corresponds to the difference of temperatures $200\frac{17}{91.8} = 37^\circ$. Thus, the temperature will be $3200^\circ - 37^\circ = 3163^\circ K$, or $2890^\circ C$.

During the calculation of the temperature of explosion it is necessary to set up in accordance with it. For a preliminary estimate it is possible to make use of the condition that for various types of explosives the temperature of explosion is associated with the heat (with a constant volume and liquid water) by an approximate linear ratio (Table 8.5).

Table 8.5. Formulas for an Approximate Calculation of the Temperature of Explosion (Q is with a Constant Volume and Liquid Water in Kilocalories per Kilogram)

Type of explosive	Approximate temperature of explosion in $^\circ C$
Non-safety nitroglycerines	$2.54Q + 280$
Safety nitroglycerines	$1.77Q + 430$
Non-safety trotyl ammonites	$1.88Q + 560$
Safety trotyl ammonites	$1.74Q + 470$
Ballistite powders	$2.1Q + 697$

If solids are encountered among the explosion products at the usual temperature, then their internal energy is derived according to the table of Appendix 9 while taking into account the fact that the melting and evaporation of heat temperature are sufficiently high. Above the critical temperature the heat capacity of vapor is accepted as equal to the heat capacity of gas with the same number of atoms per molecule. There are reliable data on heat capacities and the melting and evaporation heats of solids at high temperatures for only a few substances.

The explosion temperatures of several explosives which were calculated for the explosion equations, shown in Chapter VII (p. 584) are given in Table 8.6.

Table 8.6. Explosion Temperature of Certain Explosives*

Explosive	Temperature of explosion in °C
Trotyl	3010
Picric acid	3410
Tetryl	3700
Nitrocellulose (13.3% N)	3270
PETN [TEN = Tetranitropentaeritrit; Pentaerthrityl Tetranitrate]	4040

*Initial temperature of the explosive equal to 18°C, i.e., 291°K.

In conclusion let us note that the explosion temperature computations are based on the hypothesis that the heat capacity of explosion products is not dependent upon the pressure. This assumption is approximately correct for moderate pressures. However, as already noted in Chapter IV, at the extremely high pressures which are attained during detonation of condensed explosives with a great density, an appreciable proportion of the blast energy lies in the elastic part of the energy of molecules of the highly dense explosion products. The thermal proportion of energy is essentially less than for gases at moderate pressures, and the temperature is correspondingly lower than its value when obtained by the usual computation.

2. Experimental Determination of the Temperature of an Explosive Transformation

Attempts to measure the temperature of the burning of powders in a manometric tube with the help of a thermocouple did not give reliable results. In order to estimate this temperature Nobel detonated pyroxylin in a manometric tube with a great loading density (0.28 g/cm^3). There was a small role of osmic wire in the charge. After the explosion a layer of metal was removed from the internal walls of the tube and osmium was found in the shavings. Apparently, during the explosion the osmium was partially converted into steam, which under high pressure was diffused into steel. Inasmuch as the temperature of the melting of osmium is equal to 2500°C, Nobel assumed that the explosion temperature of pyroxylin was appreciably higher than 3200°C.

Mürauer used a similar method. For a mixture of ammonium nitrate and trotyl he set the minimum content of the latter at 7%, during which the fusion of the thin pointed platimun wire, placed in the charge was obtained. For this mixture Mürauer also set the explosive combustion pressure also in accordance with the pressure, while figuring from an equation of state, and computed the temperature of gases. Comparing the temperature of the fusion of platimum (1750°C) and the temperature, calculated by pressure with the temperature, calculated by the usual method, Mürauer arrived at the conclusion that the value of the heat capacities of Mallard and Le Chatelier are too high, a fact which was confirmed later by other researchers.

A. Ya. Apin and I. M. Voskoboynikov determined the temperature of the detonation of a number of explosives by using the optical color method of temperature measurement. This method is based on the fact that the distribution of energy is determined by a solid continuous spectrum characteristic for detonation, or the ratio of brightness when there are two wave lengths ("red-blue" comparitive method).

The relative spectral brightness of a completely dark body $b_{\lambda,\ T}$ for a wave length λ is expressed by the formula of Planck

$$b_{\lambda,T} = C_1\lambda^{-5}\left(e^{C_2/\lambda T} - 1\right)^{-1},$$

where $C_1 = 3.70 \cdot 10^{-5}$ ergs per sq cm^2/sec;

$C_2 = 1.433$ cm·degrees.

In the visible part of the spectrum, when $T < 6000^\circ K$ $e^{c_2|\lambda T} \gg 1$, and the ratio of brightnesses of the two wave lengths λ_1 and λ_2, for the given temperature T may be expressed by the proportion

$$\ln\frac{b_{\lambda_1,T}}{b_{\lambda_2,T}} = 5\ln\frac{\lambda_2}{\lambda_1} + C_2/T\,\frac{\lambda_1-\lambda_2}{\lambda_1\lambda_2},$$

whence

$$T = \frac{C_2\,\dfrac{\lambda_1-\lambda_2}{\lambda_1\lambda_2}}{\ln\dfrac{b_{\lambda_1,T}}{b_{\lambda_2,T}} - 5\ln\dfrac{\lambda_2}{\lambda_1}}.$$

The glow of the explosion of the cylindrical charge of the explosive was recorded with the help of a photomultiplier, the current of which was recorded on an oscillograph. A system of lenses was in front of the photomultiplier – an aperature which cut the glow of a limited section of the face of the charge which was opposite the end from which the initiation was produced. The explosive was placed either in a plexiglas glass with a transparent bottom (in the case of liquids), or in water (in the case of solid explosives), in order to exclude the glow from the strong shock wave in the air; by the same considerations explosives were pressed to a density which approximated specific gravity. With the help of two light filters, certain parts of the spectrum were intersected and the relative brightnesses determined in corresponding wavelength intervals. The temperature in the detonation front was computed in accordance with these data.

The measured temperatures constituted (in $^\circ$K) for hexogen ($\rho = 1.80$ grams per cu.cm) 3700°, for PETN ($\rho = 1.77$ grams/cu.cm) 4200°, for dyne ($\rho = 1.70$ grams/cu.cm) 3700°, for nitromethane ($\rho = 1.14$

grams/cu.cm) 3700°, for methyl nitrate (ρ = 1.21 grams/cu.cm) 4500°, for nitroglycol (ρ = 1.50 grams/cu.cm) 4400°, and for nitroglycerine (ρ = 1.60 grams/cu.cm) 4000°.

Comparing the data, obtained for the three liquid nitro esters which were close to the heat of the explosion, it is possible to establish that the light (ρ = 1.21 grams/cu.cm) methyl nitrate has the highest temperature of detonation and the heavy (ρ = 1.6 grams/cu.cm) nitroglycerine, the lowest. This may be connected with the fact that the detonation pressure is greater when the density is higher and that a large part of the energy in the front of the detonation wave is in the form of elastic energy; correspondingly, the proportion of thermal energy and temperature is less.

3. Burn-Out of the Barrel of a Weapon During Firing

The burning-out of the bore of the barrel of a firing weapon is closely associated with the temperature of burning. The losses of metal, which are carried away during firing by heated and compressed gases are extremely great. Thus, according to Siva's calculations around 1/3 of a kilogram of metal flies out with the gases when a 28-cm gum is fired.

The burn-out usually appears first on the connecting cone of the part of the barrel, to which the projectile is joined by the rotating band. It facilitates the process wherein the cone and adjacent projecture continue to move further toward the muzzle and the volume of the combustion chamber is increased. The diameter of the bore is simultaneously increased. As a result of this there is a decrease in the initial velocity and range, and also an increase in dispersion. The end result is a reduction of the ballistic life of the weapons. Certain powerful guns lose their ballistic properties after several hundreds or even dozens of firings as a result of burn-out.

Application of powders with a lower temperature of burning leads to a decrease of burn-out. Thus, according to Gal'vits, during a transition from nitroglycerine powder with a burning heat of 950 kilocalories per kilogram to powder with a combustion heat of 820 kilocalories/kg, the life of artillery barrels is increased approximately 1.5 times, but during transition from the latter to low-calorie (690 kilocalories/kg) diglycolic powder, by 10 times. Therefore, lowering of the temperature of the burning of powder by changing its composition or by other methods is the basic means of increasing the life of the gun barrels.

The basic factor determining burn-out is, according to D. K. Chernov, the temperature, which is attained during combustion. Strong and brief heating of the surface of the bore during its repeated use gives rise to the formation of a network of cracks on it, as a result of which the metal is easily broken off by the moving projectile and flow of gases. Increase of pressure intensifies the heating-up of the barrel by gaseous combustion products and increases the loss of metal during firing.

The nature of the powder also has an effect on the intensity of erosion. Nitroglycerine powders during equal caloricity cause greater burn-out than pyroxylin, which fact may be associated with the differences in the composition of intermediate, and also the end combustion products which interact with the metal of the barrel.

Laboratory research of burn-out is accomplished with the aid of an erosional bomb (Fig. 8.4). In addition to the two plugs, of the usual manometric tube (see p. 641) this bomb has a third plug, which screws into the wall. A small metallic cylinder is fastened in this with a narrow central channel, through which hot gaseous combustion products exit during testing. Decrease in the weight of the cylinder during the experiment serves as a measure of the burn-out. An instrument may be applied both for a characterization of the erosional capacity of the powder as well as a characterization of the stability of the metal in relation to the burn-out. Experiments showed that the magnitude of burn-out is essentially dependent upon the combustion temperature. Thus, maximum loss in weight of the cylinder was observed during the burning of nitrogelatin, nitromannite, and nitroglycerin powders of the usual type. Pyroxylin powder occupied a middle position, and, finally, minimum losses of cylinder weight were produced by black powder and nitroguanidine. The above indicated explosives are arranged in the same order in accordance with the decreasing explosion temperature. Of the different metals examined the smallest weight loss of the cylinder was effected by the most refractory – platinum, and low-temperature melting aluminum and zinc showed maximum losses. The capacity for chemical reaction of the combustion products with metal also plays a major role. Thus, the research of K. K. Snitko showed that during the dilution of a stoichiometric mixture with oxygen detonating gas causes an incomparably greater burn-out of steel than when this gas is diluted with the same volumetric quantity of hydrogen.

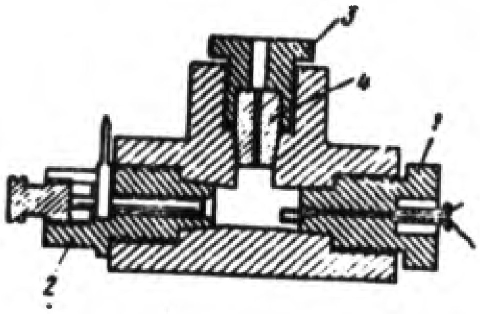

Fig. 8.4. Erosional bomb. 1 – ignition plug, 2 – crusher plug, 3 – cylinder plug of tested metal, 4 – cylinder of tested metal with central channel.

§ 3. The Explosion Pressure

It is necessary to differentiate two essentially different concepts, the combustion pressure and the detonation pressure.

Combustion pressure is that pressure which is built up by the gaseous products of the explosive burning in a partially or completely closed shell. This pressure is uniformly active in all directions. Maximum combustion pressure for a given explosive and loading conditions is attained when the latter occurs in a closed shell without external losses.

The detonation pressure is the directed pressure jump in the front of the detonation wave. The magnitude of the limited jump does not depend on the presence of the shell.

Let us picture for ourselves two identical open vessels which are half-filled with the same explosive. We shall start the burning in the first vessel by appropriate initiation measures. Inasmuch as the vessel is open the gaseous combustion products will depart and the vessel will remain intact. We will excite an explosive detonation in the second vessel. That part of the vessel which is in direct contact with the explosive will be crushed to a fine degree, but the upper, on which the detonation pressure did not act directly, will remain unimpaired. During a repetition of the test in closed vessels both vessels will be shattered, but during the burning the splitting of walls will be uniform in contrast to the detonation during which a part of the walls of the vessel which are in contact with the explosive will be shattered.

We have examined the method of calculating pressure detonation in Chapter IV. The methods of its test determination are closely connected with a characterization of the destructive effect of an explosion and are considered in Chapter IX. Here we shall consider the factors upon which are dependent the combustion pressure of a condensed explosive and also the methods of computing its experimental determination.

1. Combustion Pressure

Combustion pressure in a closed vessel is dependent upon the volume of the gaseous products formed by the explosive, their temperature, and the chamber capacity, in which the charge is housed, i.e., upon the density of the loading. If the chamber is completely filled by the explosive then, the pressure depends on its gravimetric density. For all practical purposes, in view of the comparative slowness of the process of combustion, the pressure is associated also with the burning rate: the greater the speed, the shorter the burning time is, and consequently also the loss of heat through heat conduction and radiation. When there are smaller heat losses, the temperature of the gases and the pressure built up by them are higher.

In order to estimate the approximate value of the volume of gases and temperature for combustion pressure, let us assume that the products of transformation are in conforming with the law of ideal gases.

From the ratio

$$\frac{p_1 v_1}{T_1} = \frac{p_0 v_0}{T_0}$$

we derive

$$p_1 = p_0 \left(\frac{v_0}{v_1}\right)\left(\frac{T_1}{T_0}\right). \tag{8.6}$$

Here v_1 is the volume occupied by the explosive, v_0 is the volume of gaseous explosion products under normal conditions, $T_0 = 273^\circ K$ and T_1 is the temperature, which is attained during burning; p_0 is the constant and equals 1.033 kilograms/sq cm.

Pressure p_1 is determined by the product of two factors: the volume factor v_0/v_1, which shows a change of volume during the explosion, and the thermal, or temperature, factor T_1/T_0, which characterizes the change of temperature as a result of the chemical reaction of the explosion. In Table 8.7 we may see the values of volume and temperature factors for certain gaseous and condensed explosives.

Table 8.7. Values of Volume and Temperature Factors for Certain Explosives

Explosive	v_1 liter/kg	v_0 liter/kg	$\frac{v_0}{v_1}$	T_1 °K	$\frac{T_1}{273}$	Products of volume and temperature factors
Condensed explosives						
Black powder	0,59	280	470	2650	9,7	4 600
Nitrogelatin (92:8, of the difficult-freezing type)	0,65	715	1100	5030	18,4	20 200
Ammatol 80/20	0,95	900	950	2890	10,6	10 100
Gaseous explosives						
$2H_2+O_2$	1866	1244	0,67	from 2700 to 4000	to 14,5	from 9 to 25
$2CO+O_2$	763,8	509,2	0,67			
$C_2N_2+O_2$	533,3	800,0	1,5			
$C_2N_2+2N_2O$	479,9	799,8	1,67			

From Table 8.7 it is clear that the values of the temperature factor for gases and solid explosives are close and that the volume factor in the latter case is approximately a thousand times greater than for gases. Thus, the pressure of a gas explosion is at least one thousand times lower than the pressure of the explosion of a condensed explosive; the destructive effect is also in accordance with this. From these ratios it follows also that for an increase of the action of a gaseous explosion to an order of magnitudes, characteristic for the blast of a condensed explosive, a preliminary compression of gas to a pressure of approximately 1000 atm (tech.) is essential. Application for explosive purposes of such strongly compressed gases has still not become realistic even at the present time.

The condensed explosives given in Table 8.7, are located in that order, in which they were introduced in due time into blasting operations. We see that the development of explosives from black powder to ammonites was accompained by an increase of the volume factor; simultaneously with this, the transition from dynamites to ammonites signified a certain reduction of the temperature factor.

Absolute values of pressure, obtainable during an explosion within the capacity of the explosives themselves which are compressed to a high density, are exceptionally great. Thus, for example, during the explosion of mercury fulminate, if one were to take for it the equation

$$Hg(ONC)_2 = Hg + 2CO + N_2,$$

the volume of gaseous products exceeds by more than a thousand times the initial volume of the explosive. If one were to conceive the fact that by cooling the explosion products to a low temperature, for instance, to -200°C and transforming them into a liquid state, then in this state they will occupy a volume which is greater than mercury fulminate. Therefore, in order to reduce the liquid products of explosion to the initial volume of the explosive, it is necessary to compress them, which will require great pressure in view of the low compressibility of liquids. If one were to consider, furthermore, that during the explosion of mercury fulminate, gases have a temperature of not -200°C, but around 4000°C, then it is possible to imagine the tremendous pressure they will produce in this process. Calculations by equations of the state of real gases usually utilized for moderately increased pressures such as, for instance, by the Van der Waals equation, give pressures, equal to infinity at significantly smaller densities than is practically applicable. By indirect methods of computing combustion pressure, it is theoretically possible, as we will see below, to exceed 100,000 atm (tech.).

Combustion is utilized technologically mainly for communicating kinetic energy to projectiles. In this case not only the magnitude of the pressures plays a substantial role, but also the rate of its buld-up. During the burning of an explosive change in a closed vessel, the pressure curve as a function of time has, in general the form depicted in Fig. 8.5. At point A the gases went up to the wall of the vessel: this is followed by an accelerated rise in pressure, at point K (point of inflection), which shifts to an inhibiting stage. At point B the pressure has attained the maximum and dp/dt = 0.

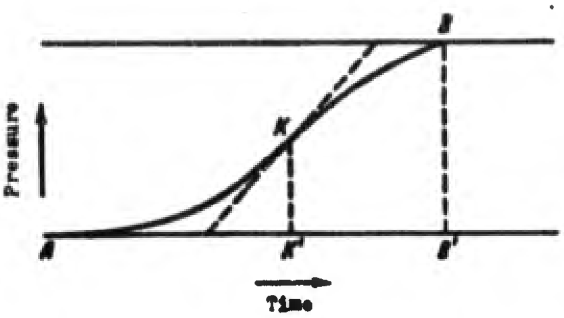

Fig. 8.5. Change of pressure in time during burning of explosive in a closed vessel.

The sharpness of the rise in presusre expressed by the ratio $\frac{KK'}{AK'}$, OR $\frac{BB'}{AB'}$, characterizes the action of the explosive. If this ratio is small, then the action is chiefly propellant, the projectile obtains acceleration without noticeable residual deformation. If, however, the above-indicated ratio is very great, then the speed, attained by the projectile during the build-up of pressure, will be less and, furthermore, if a very high pressure is attained, the projectile and the weapon barrel may be split.

The greater the propellant action of combustion is expressed, the more advantageous its ballistic use will be. This is apparent from the diagram in Fig. 8.6, which shows pressure as a function of the projectile's path in the gun bore. The kinetic energy of the projectile is characterized by the area restricted to the LMV curve. If the pressure increase rapidly to maximum value such as, for instance, on curve 2 or to an even greater degree on curve 3, than with that same area, restricted to the curve, and consequently, also to the energy of the projectile, the maximum pressure is significantly greater. An ideal, but practically unrealized case is presented by straight line HF, which produces constant pressure throughout the path of the movement of the projectile. Such a dependence shows the minimum requirements for durability of the gun barrel under the given energy of the projectile.

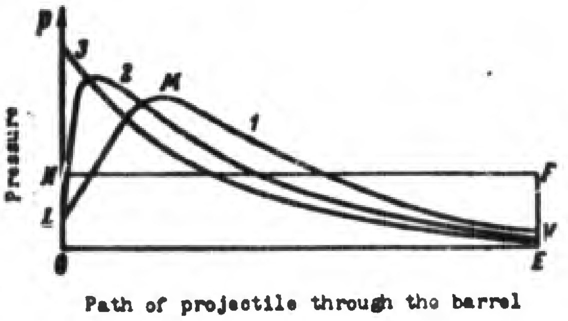

Fig. 8.6. Curves of pressure change during firing for powders of different progressiveness.

In order to arrive at this dependence, the particles of powder are given a special form so that their surface in the process of burning will remain constant or even increase (powder with multichannel grains). Gun-powder, moreover, is usually subjected to special treatment, which in powder-making is called flegmatization, and consists of the introduction of impurities (camphor) into the surface layer of the powder grain which inhibit-burning.

During the burning of a charge from flegmatized powder, after combustion of the surface layer of grain the burning rate increases, and this to a certain degree compensates for the decrease in the burning area. The ratio of maximum pressure to the average for flegmatized powder, all other things being equal, is smaller than for nonflegmatized powder.

2. Computation of Burning Pressure

Experimental study of the dependence between the loading density Δ and the maximum pressure, obtainable in a closed vessel, showed that pressure increases with the loading density, not linearly, as is required by an equation of the state of ideal gases, but faster (Fig. 8.7). Analytically, the dependence derived from the test could be expressed by the coefficient for nitroglycerine

$$p=\frac{9280\Delta}{1-0{,}723\Delta}$$

and for smoky powder

$$p=\frac{2640\Delta'}{1-1{,}06\Delta'},$$

where Δ' is the density of loading carried over to the part of the powder which is converted into gases.

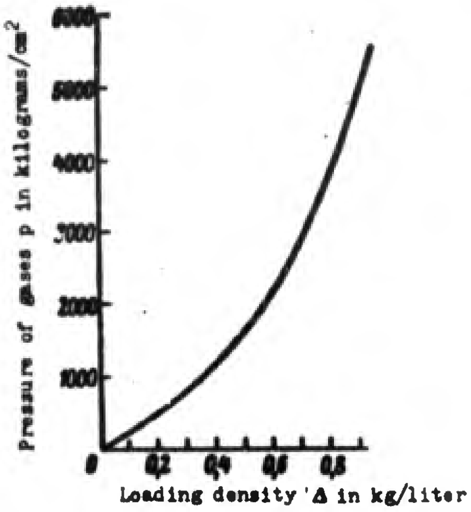

Fig. 8.7. Dependence of maximum pressure upon loading density during burning of smoky powder.

Designating coefficients under Δ in the numerator by f and in the denominator by α, we will derive in general

$$p=\frac{f\Delta}{1-\alpha\Delta}. \tag{8.7}$$

It is also easy to arrive at this ratio theoretically. For gases of great density which are produced during combustion of an explosive in a closed vessel, the equation of the state of ideal gases pv = RT is no-longer applicable. In this case it is possible to use the equation of the state of real gases of Van der Waals

$$\left(p+\frac{a}{v^2}\right)(v-b)=RT, \tag{8.8}$$

in which the term a/v^2 takes into account the gravitational force between molecules, which act as a certain "internal pressure" which compresses gas. The term b (which is designated in the theory of explosives usually by the letter α and is called "covolume") takes into account its own volume of molecules w_0 (as the theory indicates, $\alpha \approx 4w_0$). Inasmuch as a/v^2 rapidly decreases with a rise in temperature, it is possible to disregard this magnitude during calculation of the pressure of burning and to use an equation of real gases in the simplified form

$$p(v-\alpha)=RT, \tag{8.9}$$

where R for 1 kg of explosive equals $\frac{p_0 v_0}{273}$.

Designating $RT = \frac{p_0 v_0}{273}T$ by f and dividing this magnitude by $(v - \alpha)$ we will obtain

$$p=\frac{f}{v-\alpha}.$$

Since for 1 kg

$$v=\frac{1}{\Delta},$$

then

$$p=\frac{f}{1/\Delta-\alpha}.$$

Multiplying the numerator and denominator by Δ we will obtain finally the equation of Nobel and Abel

$$p=\frac{f\Delta}{1-\alpha\Delta}. \tag{8.7}$$

Magnitude f is sometimes called the specific pressure according to the following considerations. If one were to allow fulfillment of the laws of ideal gases, i.e., to take $\alpha = 0$, then when $\Delta = 1$ we will obtain $p = f$. Consequently, f numerically coincides with the pressure built up by 1 kg of explosive during combustion in a volume, equal to one liter on the condition (actually unrealistic) that the gases behave as ideal gases. Usually magnitude f is designated in accordance with its dimension by the specific energy of the explosive* and calculated from the ratio

$$f=\frac{p_0 v_0 T}{273}\ \text{liter atm (tech.)/kg.} \qquad (8.10)$$

Magnitude α is usually calculated by using the empirical ratio

$$\alpha=0{,}001 v_0, \qquad (8.11)$$

where v_0 is the volume of gaseous explosion per kilogram of explosive under normal conditions. If formed, the volume of solids is added to this magnitude. This volume can be calculated by knowing the number of moles of each of the solids which formed during the explosion of 1 kg of explosive and their molar volumes (see Appendix 10).

Both magnitudes α and f can be determined also experimentally with the help of a manometric tube from a system of two equations associated with them:

$$p_1=\frac{f\Delta_1}{1-\alpha\Delta_1}$$

and

$$p_2=\frac{f\Delta_2}{1-\alpha\Delta_2}.$$

From equation (8.7) it follows that when $\Delta_k = 1/\alpha$ the value $p = \infty$. For the majority of explosives Δ_k densities are actually attainable. However, they have only a mathematical value and in no way lead to infinitely high pressures. The fact is that α cannot be considered independently from the pressure and formula (8.11) is only approximately correct for pressures, not exceeding several thousand

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*This designation is not entirely accurate. Magnitude f, as it is easy to show, does not represent the entire energy of the explosive but only a part of it $f = (k - 1)E$, where $k = \frac{c_p}{c_v}$.

atmospheres. For higher pressures the covolume is less, however, the law of its change is unknown, and to apply the formula of Nobel and Abel in its simple form for these conditions is impossible.

For pressures, exceeding the limit of applicability of the equation of Nobel and Abel, different empirical and semi-empirical equations of state were presented.

Taylor recommends for corresponding computations the equation of Khirshfel'd and Rozevar with virial coefficients of the following form:

$$\frac{pv}{nRT}=1+\frac{b}{v}+0{,}625\,\frac{b^2}{v^2}+0{,}287\,\frac{b^3}{v^3}+0{,}193\,\frac{b^4}{v^4}, \qquad (8.12)$$

where b is the second virial coefficient at high temperatures which are calculated on the basis of definite hypotheses concerning the energy change of the interaction of molecules with a distance between them;

v is the volume of gaseous products of explosion;

n is the number of moles of these products per kg of explosive.

Values of b at high temperatures for various gases, which are usually included in the composition of explosion products are given in Appendix 11. A second virial coefficient may be calculated approximately by a summation of molar coefficients:

$$b=\sum n_i b_i,$$

where n_i is the number of moles of i-th gas which are included in the composition of explosion products; b_i is the molar coefficient for this gas.

Taking R = 0.0848 liters·atm (tech.)deg^{-1}·mole^{-1} and designating the density of the explosive by ρ, and b/v by x, we obtain

$$p=0{,}0848\,nT\rho\,(1+x+0{,}625x^2+0{,}287x^3+0{,}193x^4). \qquad (8.12a)$$

If solids are also formed in addition to gases during the explosion, then, while considering them incompressible, it is necessary, to decrease the volume in proportion to the percentage of gases for the magnitude of volume α_1 of the solids produced during the explosion of one kilogram of explosive.

Expression (8.12a) then takes the following form:

$$p = 0{,}0848 \frac{nT\rho}{\frac{1 - a_1\rho}{1000}} (1 + x_1 + 0{,}625 x_1^2 + 0{,}287 x_1^3 + 0{,}193 x_1^4). \qquad (8.12b)$$

where

$$x_1 = \frac{b}{\left(\frac{1000}{\rho} - a_1\right)}.$$

Using this expression for pressure, it is possible to calculate also for the equilibrium of the reaction of water gas G, of the coefficient, which takes into account the imperfect nature of the gases:

$$\lg G = 4{,}38 \frac{n}{b}\left(1 - \frac{a_1\rho}{1000}\right)(x_1 + 0{,}625 x_1^2 + 0{,}287 x_1^3 + 0{,}193 x_1^4). \qquad (8.13)$$

Let us consider examples of the calculation of pressure and other characteristics of explosion by the above-described methods.

1. We shall calculate the pressure which was built up while burning ammatol 80/20 with a loading density of Δ = 0.25 kg/liter. Considering that the density of loading is small, we compute while, using equation (8.7):

$$f = \frac{p_0 v_0 T}{273} = \frac{1{,}033 \cdot 898 \cdot 2890}{273} = 9820 \text{ liter atm (tech.)/kg;}$$

$$a = 0{,}001\, v_0 = 0{,}001 \cdot 898 = 0{,}898 \text{ liter/kg;}$$

$$p = \frac{9820 \cdot 0{,}25}{1 - 0{,}898 \cdot 0{,}25} = 3166 \text{ atm (tech.).}$$

2. We will calculate heat, temperature, the volume of gases and static pressure during an adiabatic transformation in its own

volume of ammonal, containing 70% ammonium nitrate 15% trotyl, and 15% aluminum with a density of 1.20 kg/liter. Taking into account the fact that the density is considerable, we calculate the thermal characteristics and pressure while considering the influence of pressure on the reaction equilibrium of the water gas.

We shall start with an approximate calculation of the explosion heat per kilogram of explosive.

Products of Explosion in Moles (by Table 8.2)

Explosive	CO_2	H_2O	N_2	O_2	Al_2O_3
Trotyl	4,620	1,650	0,990	—3,465	—
Ammonium nitrate	—	17,500	8,750	4,373	—
Aluminum	—	—	—	—4,170	2,775
	4,620	19,150	9,740	—3,260	2,775

Oxygen balance $\frac{-3.260 \cdot 32 \cdot 100}{1000}\% = -10.43\%$.

Number of moles of gases n = 33.51.

Volume of gases under normal conditions $v_0 = 22.4n = 22.4 \cdot 33.51 = 750.4$ liters/kg.

Full combustion heats under normal conditions (18°, constant volume, liquid water) by Table 8.2 are:

trotyl	0.150 kg; $q = 0.150 \cdot 3596$	539.4
ammonium nitrate	0.700 kg; $q = 0.700 \cdot 628$	= 439.6
aluminum	0.150 kg; $q = 0.150 \cdot 7382$	= 1107.3
		2086.3.

In order to account for the incompleteness of oxidation, we subtract

$$135(O_2) = 135 \cdot 3{,}26 = 440{,}1.$$

The heat of the explosion is approximately equal to

$$2086{,}3-440{,}1=1646{,}2.$$

The temperature of explosion is approximately equal to

$$t=1{,}88Q+560=1{,}88\cdot 1646{,}2+560=3665^\circ\ \text{C}, \quad \text{or} \quad \sim 3925^\circ\ \text{K}.$$

The numbers of gram atoms of elements:

$$c = (CO_2) = 4.620;$$

$$h = 2(H_2O) = 38.300;$$

$$o = 2(CO_2) + (H_2O) + 2(O_2) = 2(4.620) + (19.150) + 2(-3.26) = 21.87.$$

We now calculate the volume, occupied by gaseous products.

The volume per kilogram of explosive is:

$$\frac{1000}{\rho}=\frac{1000}{1{,}20}=833{,}3\ \text{см}^3.$$

Volume Al_2O_3:

$$a_1=2{,}775\cdot 25{,}5=70{,}9\ \text{см}^3,$$

where 25.5 is the molar volume Al_2O_3 in cu cm.

The volume occupied by gases is:

$$\frac{1000}{\rho}-a_1=833{,}3-70{,}9=762{,}4\ \text{см}^3.$$

The proportion of the volume occupied by gases is:

$$1-\frac{a_1\rho}{1000}=1-\frac{70{,}9\cdot 1{,}20}{1000}=0{,}915.$$

Let us make a calculation of the imperfectness of gases: the second virial coefficient $b(cm^3)$ of the equation of state is tentatively equal (see Appendix 11) to

$$b=n_{CO_2}b_{CO_2}+n_{H_2O}b_{H_2O}+n_{N_2}b_{N_2}=$$
$$=4{,}62\cdot 37{,}0+19{,}15\cdot 7{,}9+9{,}74\cdot 34{,}0=653{,}4\ \text{см}^3.$$

For computing G by the formula (8.13) we calculate x_1 [see formula (8.12b)] and the sum of its powers:

$$x_1 = \frac{b}{\left(\frac{1000}{\rho} - \alpha_1\right)} = \frac{653,4}{762,4} = 0,8570;$$

$$x_1 + 0,625x_1^2 + 0,287x_1^3 + 0,193x_1^4 =$$
$$= 0,8570 + 0,625 \cdot 0,8570^2 + 0,287 \cdot 0,8570^3 + 0,193 \cdot 0,8570^4 = 1,6009.$$

$$\lg G = \frac{4,38n}{b}(x_1 + 0,625x_1^2 + 0,287x_1^3 + 0,193x_1^4) \times$$
$$\times \left(1 - \frac{\alpha_1\rho}{1000}\right) = \frac{4,38 \cdot 33,51}{653,4} 1,6009 \cdot 0,915 = 0,3293.$$
$$G = 2,135.$$

For a temperature of 3925°K, according to an approximate estimate lg K is 0.916 and K = 8.24; by a correction factor we obtain:

$$K' = KG = 8,24 \cdot 2,135 = 17,60.$$

We find equation coefficients for a calculation of the composition of the explosion products (Chapter VII, page 564):

$$a = K' - 1 = 17,60 - 1 = 16,60;$$
$$b = K'\left(\frac{1}{2}h + c - o\right) + o = 17,60\left(\frac{38,30}{2} + 4,620 - 21,87\right) +$$
$$+ 21,87 = 55,31.$$
$$C = c(c - o) = 4,620(4,620 - 21,87) = -79,65;$$
$$(CO_2) = \frac{-55,31 + \sqrt{55,31^2 + 4 \cdot 16,60 \cdot 79,65}}{2 \cdot 16,60} = 1,086;$$
$$(CO) = c - (CO_2) = 4,620 - 1,086 = 3,534;$$
$$(H_2) = \frac{1}{2}h + c - o + (CO_2) = 19,15 + 4,620 - 21,87 + 1,086 = 2,986;$$
$$(H_2O) = o - CO_2 - c = 21,87 - 1,086 - 4,620 = 16,161;$$
$$N_2 = 9,740.$$

The full combustion heat (v = const, H_2O_{liq}) is 2086.3 kilocaloies.

The correction for CO_2 → CO is

$$3,534 \cdot 67,34 = 238,0 \text{ kcal.}$$

The correction for H_2O → H_2 is

$$2,986 \cdot 67,50 = 201,6 \text{ kcal.}$$

The explosion heat is

$$2086,3 - 439,6 = 1646,7 \text{ kcal.}$$

A check of correctness of the adopted value of the second virial coefficient is:

$$b = n_{CO_2} b_{CO_2} + n_{CO} b_{CO} + n_{H_2O} b_{H_2O} + n_{N_2} b_{N_2} =$$
$$= 1,086 \cdot 37,0 + 3,534 \cdot 33,0 + 2,986 \cdot 14,0 + 16,164 \cdot 7,9 + 9,74 \cdot 34,0 = 657,5.$$

Knowing the composition of the explosion products, we can calculate the temperature of explosion.

The difference of internal energies from 4000 to 291°K by calculations according to Appendices 8 and 9 constitutes:

$$\begin{aligned} CO_2 &: 1,086 \cdot 44,62 = 48,5; \\ H_2O &: 16,164 (35,68 + 10,01) = 738,5; \\ CO &: 3,534 \cdot 24,00 = 84,8; \\ H_2 &: 2,986 \cdot 22,83 = 68,2; \\ N_2 &: 9,740 \cdot 23,78 = 231,6; \\ Al_2O_3 &: 2,775 \cdot 181,3 = \underline{503,1} \\ & \qquad\qquad\qquad 1674,7 \end{aligned}$$

The difference of the internal energies is greater than the explosion heat, so we therefore, calculate this difference for the closest tabular temperature of 3800°K. It constitutes 1578.9 kilocalories. Thus, the change of internal energy by 200° is 1674.7 - 1578.9 = 95.8 kilocalories. If we accept the fact that the internal energy between these temperatures changes linearly, we obtain for a change of internal energy, equal to the explosion heat (1646.7 kilocalories), a temperature of explosion of 3942°K, which is a total of 17° higher than that which we set for ourselves in the beginning of the computation. Therefore, there is no necessity to repeat the calculation which should have been made in the case when the difference between the adopted and derived temperature was considerable. It is necessary to add that in this temperature region of the equilibrium constant of water gas the change is very slight. Therefore, during small changes of temperature there is also little change in the composition of gases and the thermal effect of the transformation.

The pressure is calculated

$$p=\frac{0,0848\cdot nT\rho}{1-\frac{\alpha\rho}{1000}}(1+x_1+0,625x_1^2+0,287x_1^3+0,193x_1^4)=$$

$$=\frac{0,0848\cdot 33,51\cdot 3042\cdot 1,20\cdot 2,601}{1-\frac{70,9\cdot 1,20}{1000}}=28\,200\ \text{kg/cm}^2.$$

3. Experimental Determination of Combustion Pressure

A manometric tube is applied to determine the combustion pressure in a constant volume. The first design of such a tube was presented by Sarrau and Vieille. This tube (Fig. 8.8) is in the form of a steel cylinder 1, which has a central channel. The channel is closed from both ends by steel bushings 2 and 3. An insulated rod 5 runs through bushing 2 and serves for the electrical ignition of the charge. In bushing 3 there is a channel with a piston 6, through which the pressure of powder gases is transmitted to a copper crusher cylinder 8 pressed between the piston head and the plug 9, which is screwed into bushing 3. During combustion of the powder charge the cylinder is compressed by the pressure of the combustion products, and the decrease of its height serves as a measure of the maximum pressure in the tube.

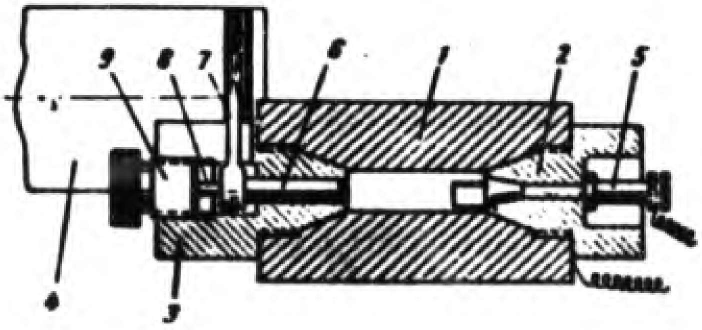

Fig. 8.8. Manometric tube of Sarrau and Vielle.

With the aid of the manometric tube it is possible to determine not only the maximum pressure, but also the change of pressure in time. For this purpose a steel pen 7, which is in contact with smutty paper fastened to a drum 4, is attached to the piston head which communicates pressure to the small crusher cylinder. During testing the drum rotates at a certain speed. This speed is measured by a sinusoid, traced on the smutty paper by a second pen which is fastened on the mount of a tuning fork which gives the known number of oscillations. As a result of the drum's rotation, the pressing of the crusher cylinder is recorded in time. After tracing, the curves (Fig. 8.9) which were produced, enable us to compute all the parameters of powder combustion on a broad scale with the aid of a comparator.

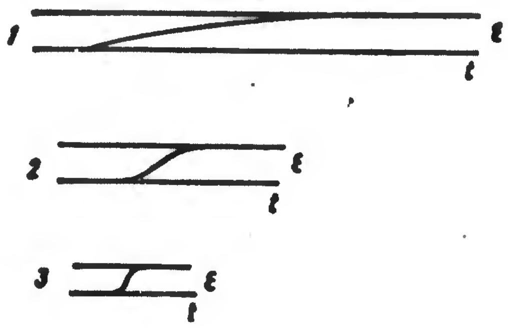

Fig. 8.9. Curves of the pressing of the crusher cylinder during testing of explosives and powders in the manometric tube. 1 — slow burning (pressed black powder), 2 — moderately fast burning (granulated black powder), 3 — fast burning (potassium picrate), time scale is increased by five times.

Weight tables are used for converting the pressing which is obtained into pressures. These tables are worked out on the bases of the results of the pressing of crushers of a given consignment on a press with varied pressures.

Research has shown that during gradually increasing pressure the dependence between the pressure and the ε pressing of the crusher is expressed by the linear ratio

$$p = K_0 + K\varepsilon, \qquad (8.14)$$

where K_0 and K for a crusher cylinder with a diameter of 8 mm and a height of 13 mm were equal to 540 and 535 with a piston weight of 60 grams during tests made by Sarrau.

If the pressure increases practically instantaneously to its maximum value, then the pressing is twice as great as during a gradual build-up of pressure:

$$p = K_0 + K\frac{e}{2}. \tag{8.15}$$

For intermediate cases, the calculation of the correction factor, which takes into account the dynamic nature of the compression of the crusher cylinder, is complicated and efforts are made to avoid it.

The increase of pressing during the instantaneous application of pressure is determined by the fact that in this case the piston attains a certain acceleration as a result of the difference between the force of the pressure of gases on the piston and the crusher resistance. The compression is therefore, continued by means of piston inertia and when the piston resistance will become equal to the pressure of gases. The smaller the mass of the piston, the less will be the inertial effect and conversely. Therefore, for intermediate cases an attempt is usually made, while decreasing or increasing the piston mass, to approach one of the extreme cases which make possible the computation of pressure by full or half pressing.

Another method of reducing the inertial effect is the preliminary pressing of the crusher cylinders in such a way that during measurement they are pressed only 0.05-0.1 mm. For this purpose the crusher cylinder was replaced by a spring and also the pressure was measured by the deformation of the steel diaphragm. Since the displacement of deformed parts by these methods are very insignificant, it is necessary to increase them by means of a mirror reflection of the light beam striking it. A recording is produced photographically.

The pizoelectric method of pressure measurement presents a radical solution to the problem. This method is based on the measurement of the electrical charge, appearing under the influence of the pressure on the surface of certain crystals (see page 521). Measurable charges are already apparent during the insignificant deformation of piezocrystal and the inertial effects in this case do not play a role.

CHAPTER IX

DESTRUCTIVE ACTION OF EXPLOSIONS

§ 1. General Concepts on Work of Explosion

The work of explosion is accomplished through the expenditure of energy (heat), released during the explosion; thus, the total energy of explosion is

$$Q=Q_0C, \tag{9.1}$$

where Q_0 is the specific heat of explosion in kilocalories/kg,

C is the weight of charge in kg, and is the most important parameter of the explosive system.

If the volume of charge v is limited (for instance by the shell or walls of blast hole), then weight of charge is

$$C=\rho v,$$

whence

$$Q=Q_0\rho v. \tag{9.1a}$$

With a fixed volume of charge, the heat of explosion is proportional specific heat and density of the explosive.

It is necessary to emphasize from the very beginning that during an explosion, as a rule, work is produced in many forms. Among them are useful forms — those, because of which the explosion is produced and useless forms, constituting a loss; with variation of conditions of explosion, the proportion of a definite form of work can change essentially.

For elucidation of the above, we will consider an explosion of charge in the ground. In this case the following basic forms of work will be produced:

1. Intense splitting and the strongest plastic flow of medium, directly adjoining the charge, and shell, if the charge was in a shell.

2. Compression, plastic flow, destruction and splitting of the medium, not directly adjoining the charge, but near it.

3. Formation and propagation in ground of elastic (seismic) waves.

4. Ejection of part of ground and formation of funnel of ejection (if charge is not too deep in the ground).

5. Formation and propagation of air shock waves (if charge is sufficiently near to surface of ground).

The sum of all work, performed by explosion, will be called <u>total work</u>. Total work constitutes part of total energy (heat) of the explosion:*

$$A_{\text{п}} = A_1 + A_2 + A_3 + \ldots + A_n = \eta_{\text{п}} E. \tag{9.2}$$

[п = t = total]

where η_t is the total efficiency of the explosion.

Further one will see that value $\eta_t = A_t/E$ is relatively large and constitutes 0.6-0.7. At the same time, the useful efficiency (ratio of useful form of work to heat $\eta_x = \frac{A_x}{E} 100$) often constitutes

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*Here and subsequently, the energy of explosion is designated by the letter Q when this quantity is expressed in thermal units, and letter E, when it is expressed in units of mechanical work. It is obvious that E(kgm) = 427Q(kilocalories).

only several percent.

With changes in conditions of explosion, the total work usually is either not changed, or is changed insignificantly; individual forms of work can vary very significantly.

Thus, for instance, if explosion of a charge is produced not in ground, but on the surface of it, then the total work practically remains equal to its former value. The work, going into the formation of the air shock wave will increase very significantly; work going into the destruction and deformation of medium, will be significantly lower; the work of ejection and formation of seismic oscillations will become practically immaterial.

In certain cases which are rather the exception than the rule, the work of explosion is produced only in one definite form. Thus, with the explosion in air of a charge without a shell all the work of explosion goes into the formation of the air shock wave. If the same charge to supply with a shell, then a certain part of the total work will be expended on the shattering and plastic flow of the shell, and also on the translation of kinetic energy to the scattering fragments.

To evaluate the magnitude of work of explosion, realized in some definite form, it is necessary to know full work of the explosion and that share of it, which under given conditions can be turned into the form in which we are interested.

A scientifically proved method of evaluating the total work of explosion was offered by I. M. Chel'tsov at the end of past century. If gas possessing internal energy U is expanded, producing work, then according to the first law of thermodynamics

$$-dU=dQ+dA. \quad (9.3)$$

The decrease in internal energy dU is equal quantity of heat, conveyed in the process of expansion to environment dQ, and performed work dA performed here. The process of expansion of gases of explosion occurs so fast that it is possible to consider it adiabatic, i.e., proceeding without heat exchange with the medium. In accordance with this, Chel'tsov used for his calculation of the work of explosion the equation of an ideal adiabatic process of expansion (let us note that in reality the process of expansion of gases of explosion cannot be considered ideal and reversible). With this assumption

$$dQ=0 \text{ and } dA=-dU=-c_v dT. \qquad (9.4)$$

For the finite quantity of work, corresponding to the total change of temperature, we have

$$A=\int_{T_2}^{T_1} c_v\,dT=\bar{c}_v(T_1-T_2), \qquad (9.5)$$

where T_1 is the initial (maximum) temperature of explosion,

T_2 is the temperature of gases at the end of expansion,

$\bar{c}_v$ is the average heat capacity in interval of temperatures from T_2 to T_1.

We will assume that $T_2 = 0$ (in real conditions expansion to $T_2 = 0$ is unrealizable), then the full maximum work A_t^* will be equal to

$$A_t^*=\bar{c}_v T_1=Q+\bar{c}'_v\cdot 290, \qquad (9.6)$$

where Q is the heat of explosion and $\bar{c}'_v \cdot 290$ is the internal energy of gas at the standard temperature of calorimetric measurements (15-20°C or 290°K).

Quantity A_t^* the maximum work, which gases of explosion can accomplish under the condition that all their internal energy is transformed into mechanical work without any remainder we will call the potential of the explosive. The quantity A_t^* can also be expressed in units of kgm/kg, for which it is necessary to multiply expression (9.6) by the mechanical heat equivalent.

Let us note that the magnitude $\bar{c}_v' \cdot 290$ is small as compared to value of heat of explosion Q; for ordinary explosives it constitutes 3-5% of A_t^*, therefore with precision, sufficient for practice, it is possible to disregard the term $\bar{c}_v' \cdot 290$ and to set

$$A_a^* \approx Q. \qquad (9.6a)$$

Disregard of magnitude $\bar{c}_v' \cdot 290$ is also possible because in real conditions, total work A_t is always significantly less than the potential A_t^* and even significantly less than the heat of explosion Q.

For full initial reserve of internal energy of n moles of ideal gas, occupying volume v_1 and having pressure p_1 and temperature T_1, we have following expressions,

$$U = nc_v T_1; \qquad (9.7)$$

$$U = \frac{p_1 v_1}{k-1}; \qquad (9.7a)$$

$$U = \frac{nRT_1}{k-1}. \qquad (9.7b)$$

Expressions (9.7)-(9.7b) are equivalent and approximately can be equated to the heat of explosion Q.

If the internal energy is set in ratio to a mass unit of gas, then, designating quantity of moles in the mass unit by n_1 and specific volume by v, we will obtain

$$U_1 = n_1 c_v T_1; \qquad (9.8)$$

$$U_1 = \frac{p_1 v}{k-1} = \frac{p_1}{\rho(k-1)}; \qquad (9.8a)$$

$$U_1 = \frac{n_1 RT_1}{k-1}. \qquad (9.8b)$$

Expressions (9.8)-(9.8b) are equivalent and approximately can be equated to the specific heat of explosion Q_0.

The expression for work of adiabatic expansion of n moles of gas may be written in the following form:

$$A = n\bar{c}_v(T_1 - T_2) = n\bar{c}_v T_1\left(1 - \frac{T_2}{T_1}\right) \approx Q\left(1 - \frac{T_2}{T_1}\right). \qquad (9.9)$$

where T_1 and T_2 are the temperatures of the products of explosion before and after expansion.

If $T_2 = T_1$, i.e., the gases are not expanded and therefore are not cooled, then $A = 0$. In the explosion of charge in a strong nonfragmentable bomb (assuming that density of loading is small and charge is suspended without touching the walls) it is possible to disregard work of formation of shock waves in the shell of the bomb. Then the work outside bomb will be equal to zero, the temperature of the gas, expanded in the bomb, will be equal to T_1, initial temperature of explosion: the internal energy of the gas will decrease with time only at the expense of heat radiation in walls of the bomb.*

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*This statement requires explanation. In the expansion of gases with accomplishment of work their temperature drops. In this case in the initial stage of expansion, the temperature of products of explosion indeed will be lowered; the internal energy partially will be converted into the kinetic energy of moving gases. Encountering the walls, the gases will be retarded and their kinetic energy once again will be turned into the internal energy of the gas. Pressure will be lower than in initial moment of explosion, but temperature will be the same, inasmuch as we assumed that work of deformation of the bomb and formation of shock waves in its walls can be disregarded. Let us suppose that instead of the charge, concentrated at the center of the bomb, we detonated the same charge evenly distributed all over volume, under the condition that heat of explosion does not change. Expansions in this case do not occur, and the temperature of gases is equal to the initial temperature of explosion. The final state of the products of explosion of the concentrated charge (after braking under the condition that identical energy was released) will be, obviously, the same as with the evenly distributed charge. Hence, it follows directly that after expansion and braking $T_1 = T_{exp}$. It is clear that if gas is in the bomb before explosion whose quantity which it is impossible to disregard as compared to the quantity of gases, forming during the explosion, then the temperature after mixing is $T < T_{exp}$.

In general, value of T_2 is difficult to estimate even approximately, therefore expression (9.9) cannot be used for practical purposes. We will transform it, introducing instead of the ratio of temperatures the relation of volumes. From the equation of the adiabatic curve

$$pv^k = \text{const}$$

and equation of state of an ideal gas we obtain

$$\frac{T_2}{T_1} = \left(\frac{v_1}{v_2}\right)^{k-1}. \tag{9.10}$$

Substituting (9.10) in (9.9), we obtain

$$A = n\bar{c}_v T_1\left[1 - \left(\frac{v_1}{v_2}\right)^{k-1}\right] = \frac{nRT_1}{k-1}\left[1 - \left(\frac{v_1}{v_2}\right)^{k-1}\right] \approx Q\left[1 - \left(\frac{v_1}{v_2}\right)^{k-1}\right]. \tag{9.11}$$

Precisely in such a form – (explicit function of ratio of initial (v_1) to final (v_2) of specific volumes) – the formula for work of gases of explosion and was given by I. M. Chel'tsov.

The ratio of volumes is practically more convenient than the ratio of temperatures, in a number of problems, the values of the final volume v_2 can be directly determined or calculated.

For certain problems, however, it is still more convenient to operate by not of volumes, but of pressures. From the equation of the adiabatic curve and expression (9.10), we will easily find

$$\frac{T_2}{T_1} = \left(\frac{p_2}{p_1}\right)^{\frac{k-1}{k}}; \tag{9.12}$$

consequently,

$$A = Q\left[1 - \left(\frac{p_2}{p_1}\right)^{\frac{k-1}{k}}\right]. \tag{9.13}$$

Here p_1 is the initial pressure of gases of explosion and p_2 – their pressure, when they, being expanded, accomplished work A. From expressions (9.2), (9.11) and (9.12) it is obvious that

$$\eta_t = \frac{A_t}{Q} = 1 - \left(\frac{p_2}{p_1}\right)^{\frac{k-1}{k}} = 1 - \left(\frac{v_1}{v_2}\right)^{k-1}. \qquad (9.14)$$

On Fig. 9.1 is shown the dependence of the ratio of total work to heat of explosion $A_t/Q = \eta_t$ on the degree of expansion for various values k (from 1.10 to 1.25). With infinite expansion ($p_2 \rightarrow 0$) the curves with various indices of the adiabatic curve asymptotically tend to one limit $\eta_t \rightarrow 1.0$, however for a certain finite value p_1/p_2 the quantity η_t increases in proportion to k. The ratio of values of η_t for curves with various k with identical expansion ratios is in inverse proportion to p_1/p_2.

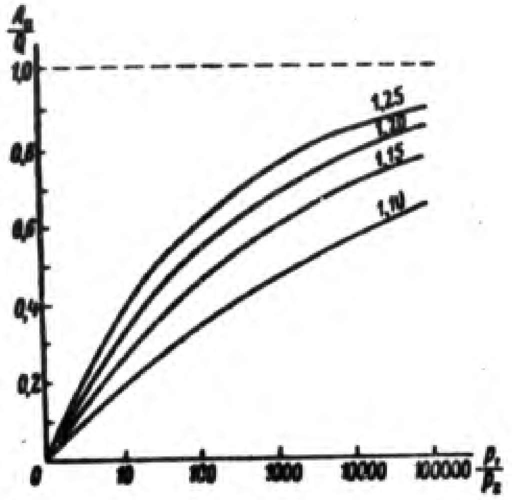

Fig. 9.1. Dependence of ratio of total work to heat of explosion on degree of expansion. Every curve corresponds to the value of k shown on the right.

The quantity

$$k = \frac{c_p}{c_v} = 1 + \frac{R}{c_v}$$

depends on the properties of the products of explosion. If, for instance, in the products of explosion 2/3 of the molecules are diatomic (CO, N_2, H_2) and 1/3 – triatomic (CO_2, H_2O), for instance, in the products of explosion of hexogene, then k = 1.25, if this relationship is inverse, i.e., in the products there are 2/3 triatomic and 1/3 diatomic molecules (nitroglycerine), then average c_v will be large, and value k will drop to 1.20. If in the products of explosion there is a significant quantity of tetratomic or pentatomic molecules, then value k will drop still more and for a given p_1/p_2, η_t will decrease. To this it is necessary to add that with an identical heat of explosion, the speed of detonation and initial pressure of products of explosion p_1 will be larger for that explosive, for which these products consist of molecules with a small quantity of atoms. If expansion goes to the same value p_2, then the ratio p_1/p_2 for such an explosive will be larger, and the work will increase somewhat as compared to an explosive, generatoring "polyatomic" products.

Quantity η_t decreases especially strongly (and, consequently, with the same energy, the work as well), if in the products of explosion there is a condensed phase (Al_2O_3, NaCl, SiO_2, etc.). Quantity k can be lowered to values 1.15, 1.10 and even 1.05 (the mixture $KClO_3 + 2Al \rightarrow Al_2O_3 + KCl$). The quantity η_t will be accordingly significantly lowered.

Let us note that still at the end of the 19th century Berthelot proposed to estimate magnitude of work of explosion per unit of weight by the so-called characteristic product Q_0V_0, where Q_0 is specific heat of explosion and V_0 is specific volume of gases. Actually Berthelot considered that $\eta_t \sim V_0$, instead of the correct relationship

$$\eta_t = 1 - \left(\frac{v_1}{v_2}\right)^{k-1} = 1 - \left(\frac{p_2}{p_1}\right)^{\frac{k-1}{k}}.$$

It is necessary to note that if number of atoms in the molecules of the products of explosion decreases, then V_0 usually increases, but from this rule there are essential exceptions (for instance, when in the products of explosion there are heavy atoms: lead, mercury, etc.) and, furthermore, character of increase of V_0 differs from character of increase of $1 - (v_1/v_2)^{k-1}$. Therefore sometimes the use of the characteristic product can give a rough approximation to reality; more frequently, however, this leads to an erroneous evaluation of efficiency of that or another explosive.

In evaluating of efficiency one should not also use the so-called "specific energy," the quantity

$$n_1RT=(k-1)Q,$$

constituting the work of isothermal expansion of gases of explosion; the work of explosion is more correctly described by the adiabatic process.

Let us return to the expression for the work of explosion in the form (9.13). Let us assume that the explosion occurs in air, and estimate the total efficiency, assuming that the expansion proceeds to atmospheric pressure, i.e., to $p_2 = 1$ kg/cm^2.

Then,

$$A_t=Q\left[1-\left(\frac{1}{p_1}\right)^{\frac{k-1}{k}}\right]=Q-q \qquad (9.15)$$

The difference $Q - A_t = q$ constitutes that heat, which even with an ideal process remains in the products of explosion after achievement by them of atmospheric pressure. Essentially, q is lost heat: it is present in gases, the pressure of which is equal to the external pressure, they no longer can be expanded and accomplish work. This afterheat produces the glow of the cloud of products of explosion after their expansion. Expanded products fast cease to glow due mixing and heat exchange with surrounding cold air.

If the explosion occurs in a solid medium with significant resistance, then expansion will stop not at 1 kg/cm^2, but at a higher pressure, depending on the properties of medium. Let us assume that $p_2 = 100$ kg/cm^2, then

$$A_t=Q\left[1-\left(\frac{100}{p_1}\right)^{\frac{k-1}{k}}\right];$$

total work will decrease, and the afterheat

$$q=Q-A_t$$

will increase.

In Table 9.1 are given the total works of explosion for 1 kg of a certain explosive with expansion to p_2 = 1 kg/cm^2, calculated by the formula (9.15).

Table 9.1. Total Efficiency of Certain Explosives with Expansion to Atmospheric Pressure (Explosives are Listed in Order of Increasing Efficiency)

Explosive or mixture	ρ g/cm^3	Q_v kcal/kg	$k=\frac{c_p}{c_v}$	η_t %	A_t kcal/kg	$\frac{Q}{Q_{TNT}}$	$\frac{A_t}{A_{tTNT}}$
Lead azide	3,8	360	1,19	77,6	280	0,36	0,33
Ammonium nitrate	0,9	380	1,30	86,2	327	0,38	0,39
Safety ammonite No. 8	1,0	710	1,20	77,5	550	0,70	0,65
Trotyl (low density)	0,9	830	1,24	82,5	685	0,82	0,82
Dynammon D	1,0	920	1,24	83,6	770	0,91	0,92
Ammonite No. 9	1,0	940	1,245	83,9	788	0,93	0,94
Trotyl (large density)	1,5	1010	1,23	83,3	840	1,00	1,00
Ammonite No. 6	1,0	1030	1,24	83,7	850	1,02	1,01
Dynamite 62%	1,45	1290	1,175	76,0	980	1,28	1,17
Alumite No. 1	1,00	1270	1,20	79	1000	1,26	1,19
Hexogene (low density)	1,00	1270	1,25	84,5	1070	1,26	1,28
Hexogene (high density)	1,60	1300	1,25	86,6	1125	1,29	1,34
Pentaerythritol	1,60	1360	1,215	82,7	1125	1,35	1,34
Elementary ammonal (20% aluminum and 80% ammonium nitrate)	1,00	1580	1,16	72,4	1140	1,56	1,36
Nitroglycerine	1,60	1480	1,19	79,7	1180	1,47	1,40
Tetranitromethane/benzene (87.5/12.5)	1,48	1650	1,18	78,5	1310	1,63	1,56

Subsequently the total work, referred to a unit weight of the explosive (specific work), we will call efficiency. In calculations of the efficiency it is necessary to know p_1, the maximum pressure of explosion. Inasmuch as expression (9.15) for calculating the efficiency is combined with the application of perfect gas laws, we considered it possible to calculate p_1 as for an ideal gas, not introducing a correction for covolume. With introduction of such correction the values of k and η_t would be changed. The real values

η_t, are apparently, below those given in Table 9.1.

As follows from Table 9.1, for many explosives, the value of η_t oscillates fluctuates within 83-85%, i.e., practically equally. For such explosives (trotyl, hexogene, ammonite No. 6, ammonite No. 9, dynammon D, Pentaerythritol) the ratio efficiencies is the same as the ratio of heats. Within the limits of a given group of explosives, efficiency can be estimated directly from the specific heat of explosion. However for many other explosives, the properties of products are such that for them the value of η_t is less (safety ammonite No. 8, dynamite 62%, alumite No. 1, nitroglycerine, mixture of tetranitromethane with benzene and, especially, elementary ammonal); the relative efficiency of such explosives is less than relative heat of explosion.

Above it was already noted that η_t is strongly lowered in the presence in the products of explosion of a condensed phase,* therefore in general it is more correct to compare the effects of explosion not by the ratio of specific heats, but by the ratio of total efficiencies.

The values of η_t given in the table are calculated according to the theory of expansion of an ideal gas with use of ideal values $k = c_p/c_v$. In the real process of expansion, the index $k' < c_p/c_v$

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*There is an exception from this general rule. In the products of explosion of trotyl is a condensed phase (carbon); nonetheless, for it the values of k and η_t are the same as for explosive whose products of explosion consist completely of gases. The fact is that gasiform products of explosion of trotyl consist largely of diatomic molecules; if in their composition there was not a suspension of carbon then the values of k and η_t for trotyl would be higher than for such explosives as hexogene, ammonite, etc. Furthermore, carbon possesses low heat capacity.

and value of the efficiency are correspondingly less. Thus, for instance, from a number of experimental data (the energy of shock wave near charge and magnitude of work in a lead bomb) it follows that for such explosives, as trotyl, hexogene, ammonite No. 6 etc., total efficiency (η_t) with expansion to atmospheric pressure constitutes not 83-85%, but 65-75%; thus, (uner the most favorable conditions) a maximum of 2/3 or 3/4 of the heat of explosion can be turned into work; the remaining energy constitutes thermal losses, the heat of working gases.

It is important to note the following; the consideration of real conditions leads to a lowering of absolute value of the work; however, the ratios of efficiencies $A_t/A_{t\ TNT}$ besides change immaterially, and these relative values, obtained from ideal theory, may be used in practice for the quantitative comparison of the effect of explosion of individual explosives.

It might seem that the presented picture of continuous expansion of gases contradicts that widespread concept, according to which products of explosion inflict the strongest impact on the medium; in reality there is no contradiction here; it is necessary only to recall that expansion occurs at such high speeds that it is possible to consider it as an impact. With expansion in air, a gradually weakening impact is inflicted in reality; with expansion in the ground, it is possible to suppose that, repeatedly being reflected from walls of explosive chamber, gases of explosion inflict a number of blows and their summation in limit gives the same result, as work of continuous expansion. Let us emphasize that in all conditions the transformation of initial energy of chemical transformation into work occurs not instantly, but during a certain, though very short time.

§ 2. Forms of Work and the Energy Balance During Explosions

As was already noted above, the work of explosion usually is produced in many forms. The natural tendency is to unite separate forms of work in groups.

In the science of explosions the division of forms of work into general, or high-explosive, action and brisant (splitting) action of explosion has long since been adopted. This breakdown, being very conditional and often insufficiently definite, at the same time has an essential basis.

The magnitude of work in forms of general action, manifested at some distance from the charge, is determined by total energy released during an explosion.

Work in the forms of brisant action is accomplished in direct proximity to the surface of the charge; its magnitude is determined by density of energy in front of detonation wave, which in turn is proportional to magnitude $\rho_0 D^2$, where ρ_0 is the density of the charge and D is the speed of detonation.

Thus, the basic parameters, determining destroying action of explosion, are, for general action – the total energy of explosion Q, and for brisance – the density of energy $\rho_0 D^2$ (for certain probelms, as we will see further, $\rho_0 D$ or CD are essential, where C is the weight of charge).

It is clear that inasmuch as there is not clear-cut boundary between high-explosive action and brisance, there is a form of work with an intermediate character of the dependence on basic parameters.

Let us consider more specifically the actual forms of work from the point of view of their dependence on basic parameters. On the total energy of explosion E depend (and, consequently, are forms of work of general action) such form of work, as destructions, producible by shock waves in air, water, ground, and also the movement of significant volumes of medium, as a result of explosions. The energy, released in an explosion, determines both the magnitude of the zone of destruction, and the intensity of destructions at a given distance. On the total energy depend also such important forms of work as the volume of thrown-out ground in the case of earth-removal explosions volume of destroyed (crushed) ground with detonation of charges in a medium (in blast holes, chambers etc.), and volume of the "crater" (expansion in medium, formed by gases of explosion).

Here it is necessary to make the qualification that in accordance with what was said in § 1, one should have used not total energy, but total work. However, as we saw, for the majority of explosives utilized in practice, the properties of the products of explosion are similar, and total work constitutes practically an identical share of total energy of explosion. Therefore, henceforth we will as the basic characteristic use the total energy or the value of the trotyl energy equivalent, excluding that case when properties of the products of explosion differ noticeably.

Regarding the destructive action of shock waves, then, as was already said, the basis of theory presents is the law of similarity of explosions, which has been very widely checked both in practice and in laboratory experiments for model charges, as well as under field conditions with the use of very big charges. In accordance with the similarity law (see Ch. VI), the distance R, at which is obtained a certain fixed value of excess pressure at the front Δp^* (which, for instance, determines the boundaries of destruction), is given by the equation

$$R=\bar{R}^{*}\sqrt[3]{C_{\text{экв}}}, \tag{9.16}$$

[ЭКВ = eq = equivalent]

where $\bar{R}^{*}$ – value of the above distance, corresponding to a given Δp^{*}.

With an explosion in a homogeneous medium, the volume enveloped by destruction of definite intensity, $v \sim R^3$; from this it follows that $v \sim C_{eq}$, the volume of destructions, is proportional to the trotyl equivalent of detonated charge. Formula (9.16) resolves the question about the boundaries of destruction, i.e., about the space, enveloped by destruction.

If we are interested in the intensity of the shock wave, and the value of Δp, then according to the law of similarity for explosions,

$$\Delta p=f(\bar{R}). \tag{9.17}$$

Equations (9.16) and (9.17) are valid not only for air (examples of application of the similarity law to air shock wave were considered in Chapter VI), but and for other media. Everywhere the basic parameter, determining destroying action of shock wave, is the total energy of explosion.

In considering the destroying action of the shock wave, we frequently proceed from an incorrect premise, trying to connect the characteristics of the shock wave directly with parameters of the detonation wave, which is patently wrong. The parameters of detonational waves are important for brisance manifested on the boundary of charge under conditions when the medium is acted upon precisely by the products of detonation. At a certain distance from charge, destructions are determined by shock wave, its energy, pressure, impulse, etc., or motion of the medium. In turn shock wave energy or energy of motion of the medium constitutes a certain share of total energy of explosion (it is clear that depending on the properties of the medium, the conditions of explosion, etc., this proportion may differ).

In case of an explosion in a solid medium, not only the products of that part of charge, which are in contact with the medium and convey to it the "primary impact" participate in forming the shock wave, but also the products of explosion of the entire charge, acting on the medium like a kind of piston. Precisely for this reason, energy of the shock wave constitutes a definite share of the total energy of the explosion and the basic parameter of the similarity law for explosions includes the total energy of explosion, expressed directly or in the form of the trotyl equivalent. In Chapter VI it was shown that the basic parameter of the similarity law is preserved also in case of explosions of another form and a physical nature other than the explosion of an explosive. A powerful spark, for instance, will form a shock wave, whose characteristics (and consequently, whose destructive action) are determined basically by the quantity of energy released by the spark. If in cases of explosion of an explosive and spark the energies are equal, then in direct proximity from the focus of the explosion the effects will be essentially distinct (in particular, a spark in air will possess incomparably lesser brisance), but at a certain distance shock waves and destruction producible by them will be practically equivalent. Certainly, everything said above is valid in the case where energy release in the explosion (in particular, in the spark) occurs at a sufficient rate. With too slow energy release, the shock wave either will not be present, or it will be weak, not corresponding to the total quantity of released energy. In the case of detonating explosives, the speed of energy release fully is sufficient and in general, not very substantial distinctions in the rate of detonation of various explosives practically do not affect the amount of energy, transformed into the shock wave.

In case of such forms of work, the expansion of cavity in a medium of the ejection of rock, a decisive role is played by not so much the shock wave, as the motion of significant volumes of the medium during the explosion, which also depends on the total energy of explosion. As the latter increases, the energy of the shock wave, as well as the energy of motion of substantial volumes of the medium, appearing usually after the passage of shock wave, also increase.

As follows from relation (6.38)-(6.40), the volume of expansion in medium (volume of water) v is proportional to the weight of the charge,

$$v = KC. \tag{9.18}$$

In the use of various explosives, by weight C we understand the value of trotyl equivalent C_{eq}.

An analogous proportionality to the weight of the charge also holds for the volume of the ejected rock. In view of the great practical importance of this question, we will consider it in greater detail.

Let us expound basis of method of calculating ejection charges. In calculations we usually assume that the ejection funnel constitutes a cone, in vertex angle of which the charge was detonated (Fig. 9.2). The ejection funnel is characterized by the ratio of its radius r to the depth W, called also the line of least resistance (LLR). The

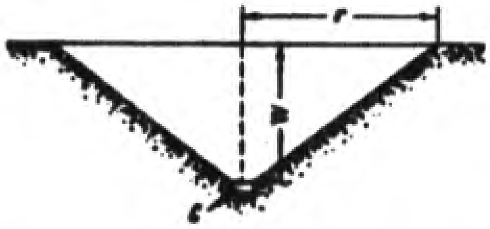

Fig. 9.2. Diagram of ejection funnel. C — explosive charge, W — line of least resistance, r — radius of funnel.

ratio

$$\frac{r}{W}=n$$

will be called the <u>index of explosive action</u>. The funnels, for which

$$n=\frac{r}{W}=1,$$

are called funnels of <u>normal ejection</u>, funnel, for which n > 1, called funnels of <u>intensive ejection</u>.

In the calculation of ejection charges the initial funnel is the funnel of normal ejection. Its volume is

$$v_{\text{норм}}=\frac{\pi}{3}r^2W\approx W^3. \qquad (9.19)$$

[норм = norm = normal]

The weight of charge, necessary for a given LLR to obtain a funnel of normal ejection, is equal to

$$C=Kv_{\text{норм}}\approx KW^3. \qquad (9.20)$$

Already from the form of formula (9.20) it follows that this old formula of explosive matter, obtained empirically in its own time essentially constitutes a special formulation of the similarity law for explosions. Coefficient K (weight of charge, necessary for ejection of a unit volume of ground) depends first of all on the properties of the ground (and also from properties of the explosive) and is determined by experimental means. In Table 9.2 are given values of K for certain grounds and rocks according to the data of Glavvzryvprom*

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*Glavvzryvprom (Glavnoye Upravleniye Vzryvnoy Promyshlennosti — Main Administration of the Explosive Industry) [Ed. Tr. note].

these values pertain to definite explosives (ammonite No. 9). With the use of other explosives, the quantity C constitutes the equivalent weight of ammonite No. 9.

For weak grounds, 1 kg of explosive produces approximately one cubic meter of ejection. With transition from vegetative soil to the strongest granite, K increases only by a factor of 2, although the difference in durability and hardness is huge. The cause lies in the fact that the basic share of the work of ejection is expended on surmounting inertial forces, determined by specific gravity, which for various grounds differ comparatively little.

Table 9.2. Value of Coefficient K in Formula $C = KW^3$

Type of ground	Coefficient K in kg/m^3
Sand, vegetative soil, peat	0.95
Clay, loam, gravel	1.10
Carbon, soft limestone, chalk	1.25
Sandstone Clay, schists	1.40
Limestone, sandstone	1.50
Dolomite, limestone strong, marble	1.60
Granite coarse-grained, dolomite strong	1.70
Gneiss, very strong limestone	1.80
Medium-grained granite, diabase	1.90
Fine-grained granite, diorite, quartz	2.00
Basalt, gabbro-diabase	2.20

If by conditions of work, ground ejection is not required, but it is necessary only to destroy or loosen the ground, in a volume, close to the volume of normal-ejection funnel, then it is necessary to have a smaller charge than for ejection. According to experiments performed by Glavvzryvprom, the charge of normal splitting is approximately 1/3 of the charge of normal ejection:

$$C_{\text{дроб}}=\frac{1}{3}KW^3. \qquad (9.21)$$

[дроб = splt = splitting]

Formula (9.21) is valid for charges near the surface and takes into account reflection from the surface; with the explosion of a charge of camouflet, the volume of destroyed rock will be less. In any case, with destruction of significant volumes of the medium, hundreds of times exceeding the volume of charge, the magnitude of the destroyed volume is proportional to the total energy of explosion, this is confirmed by direct experiments.

Charges of intensive ejection are calculated by the formula

$$C=KW^3f(n). \qquad (9.22)$$

As the basis we take the charge of normal ejection, which we multiply by the function of index of explosive action f(n). According to M. M. Boreskov,

$$f(n)=0{,}4+0{,}6n^3,$$

so that,

$$C=KW^3(0{,}4+0{,}6n^3). \qquad (9.23)$$

Formula (9.23) is usually called the Boreskov formula. Experience with mass explosions for ejection, at which the value of W attains several tens of meters, while the weights of separate charges are measured in hundreds of tons and more, showed that with such LLR the Boreskov formula gives excessively low values of C.

G. I. Pokrovskiy correctly noted that formulas (9.20)-(9.23) actually account for only the volume of ground, which it is necessary to displace: precisely the volume is proportional to W^3. During ejection, however, this ground should be lifted to a height proportional to the LLR, i.e., W. Threrfore, one would think that with the observance of similarity the weight of charge, necessary for producing funnel with a given n, must be expressed by the formula

$$C=K'W^3Wf(n)=K'W^4f(n). \tag{9.24}$$

According to Pokrovskiy, with W $\geq$ 20 m, the weight of charge of ejection is given by formula

$$C=K_1\gamma W^{7/2}(1+n^2)^2, \tag{9.25}$$

where K_1 is a constant coefficient, and γ is the specific gravity of rock.

Let us note that if in the Boreskov formula we introduce the simple additional coefficient (0.95 + 0.05 W), then formula

$$C=K(0{,}95+0{,}05W)W^3(0{,}4+0{,}6n^3) \tag{9.26}$$

gives satisfactory results both with small and with substantial W. The right side of (9.26) can be represented in the form of sum of two terms. The first of them, which includes W^3, corresponds to the work of plastic flow which is useless for ejection, concussion, e c. The second term containing W^4, is proportional to the work of ejection proper. With increasing W, share of the work of ejection increases rapidly.

Let us turn to the forms of brisance of explosions. Here it is necessary from the very beginning to note that whereas the question about the appraisal of general action of explosion may be comparatively clear, then with respect to brisance, full clarity is not yet assured.

It is possible only to note that work in form of brisance, i.e., work, accomplished on the boundary of the charge at the initial moment of expansion of the products of explosion should be proportional not to the total energy of the charge, but to the density of energy in the front of the detonation wave. In turn, the density of energy in front of the detonation wave is proportional to the pressure of detonation, i.e., is approximately proportional to the product $\rho_0 D^2$. Indeed, as we saw in (p. 347), $p_{det} = \frac{\rho_0 D^2}{k + 1}$. On the other hand, according to (9.7a), the internal energy of the compressed gas is

$$U = \frac{pv}{k-1}.$$

Setting v = 1, we obtain for the energy per unit volume

$$U_{v=1} = \frac{p}{k-1} \approx \frac{\rho_0 D^2}{k^2-1}.$$

To this it is necessary to add that the kinetic energy per unit volume of the moving products of detonation $\rho_0 w^2/2$ is also proportional to the expression $\rho_0 D^2$. Therefore, the total energy per unit volume of the products of detonation, interacting with the medium and, in particular, with their reflection, taking into account the motion of products, should be also proportional to $\rho_0 D^2$, to which is proportional both the pressure of the proceeding detonational wave, and also the pressure of the reflected wave

$$p_{отр} \approx 2{,}35 p_{дет} \qquad (9.27)$$

[отр = ref = reflected; дет = det = detonation]

Very strong fragmentation, the basic form of brisance, depends not so much on the applied energy, as on the magnitude of the effective force. In contrast to a widespread view, the share of energy, expended even on the strongest fragmentation, is small. In order to tear a solid body, it is necessary to apply a large force, but this force acts on a very short path on the order of molecular dimensions. Therefore, the magnitude of work, equal to the product of the force by the path length, is very moderate (the work of plastic flow accompanying fragmentation can be significant). Precisely for this reason, fragmentation action is determined rather by the magnitude of pressure, while the total energy, expended on all forms of brisance is small. If the pressure is small, then fragmentation action will be very weak, although the medium may have been acted upon very high energy. The foregoing does not contradict the above position that brisance is determined by the energy density in the detonation wave. We already saw that energy density and pressure developed during detonation, as in the case of the forward detonation wave and its reflection, are proportional and differ by a constant coefficient.

Thus, we arrive at the conclusion that the magnitude of work in the forms of brisance is approximately determined by the expression

$$A_{бр} = K^{*} \rho_0 D^2. \qquad (9.28)$$

[бр = br = brisance]

If we are interested in the magnitude not of work, but the impulse (or a portion there of), or in the value of the velocities of the medium bordering on the charge, then as the criterion of action of explosion we should take the parameter $\rho_0 D$. The same parameter is basic for the determination of the magnitude of the impulse, which is conveyed to the stand (pad) by the open charge. Such a case is frequently called the <u>local</u> action of the explosion.

P. F. Pokhil and M. A. Sadovskiy have recommended the following formula for evaluating the magnitude of impulse, produced by the local action of the explosion of an open charge on the stand:

$$J = \xi \frac{C}{g} \frac{D}{k+1} \frac{S_{\text{к}}}{S_{\text{п}}}, \qquad (9.29)$$

[к = c = contact]

where ξ is a constant coefficient;

C is the weight of charge;

g is the acceleration due to gravity;

D is the speed of detonation;

k is the index of politropy of the products of detonation;

S_c is the area of contact of the charge with the stand;

S_t is the total surface of the charge.

The basic characteristic of the charge in this case is the product CD. For charges of constant volume, the role of the basic characteristic will be played, obviously by the product $\rho_0 D$.

Thus, it is possible to note that whereas the work in the forms of the general action of explosion does not depend directly on the speed of detonation, the brisance, determined by properties of products of detonation, depends on its speed.

Till now, both for local, and for brisance action, we essentially considered the question of the intensity of action and the degree of manifestation of this or that form of work at a given distance from a charge of constant volume. Let us assume now that without changing the parameters ρ_0, D, k, etc., we increase the volume of charge under the condition of preservation of similarity of form. Then the volume included the fragmentation or local action of a given intensity, will increase proportionally to the volume of charge, i.e., proportionally to its weight. Thus, with respect to the volume of the medium, enveloped by destruction of a given degree of intensity, general, local, and fragmentation action are not distinguished: volumes of destruction are proportional volume of charge or its weight; the linear distances to the boundaries of the corresponding destructions have to be proportional to $\sqrt[3]{C}$.

We will consider one method of evaluating brisance which once had wide acceptance. At one time Kast proposed to estimate brisance by the "power" of an explosion. For calculating "power" per unit volume, Kast recommended following formula:

$$L = \frac{A''\rho_0}{t},$$

where A" is a quantity, proportional to the product n_1RT the "specific energy;"

t is the duration of explosion.

Kast suggested that 1/t be replaced by the proportional value of speed of detonation D. As a result, brisance according to Kast is

$$B = A''\rho_0 D.$$

Snitko modified the formula of Kast, introducing instead of A", the specific heat of explosion Q_v, and setting $t = \frac{l}{D}$ (where l is the length of the charge), obtaining thus expression $\frac{Q_v \rho_0 D}{l}$.

For a charge of constant volume, we will obtain criterion $Q\rho_0 D$, which, of course, is more preferable than the Kast expression. Sometimes attempts are made to construct a criterion, essentially close to the criterion of Snitko in which instead of Q_v there appears the magnitude of the efficiency, definite by method of the lead bomb (see below).

Is not excluded that for certain forms of work near the charge, the Snitko criterion or some other one, close to it, can give passable results, at least because it is in a certain measure intermediate between the basic characteristic of general action ($Q = CQ_0$) and characteristic of brisance, into which there enters the speed of detonation. It does not follow, however, that one should use as a universal criterion $Q_v \rho_0 D$, nor as a criterion containing efficiency instead of the energy of explosion. Experience shows that for such highly important forms of work, as destructions produced by shock waves, destructions producible by motion of the medium, ejection, fragmentation of significant volumes of the medium, and expansion of a cavity in the medium, i.e., for all forms of general action, the magnitude of the work does not depend directly on the speed of detonation.

In evaluating general action of detonating explosives, it is not the distinctions in the speed of detonation which are important, but distinctions in the reserve of energy in the given systems. Therefore, criterion $Q_v \rho_0 D$ for the forms of general action is unsatisfactory. In exactly the same way, this criterion is not satisfactory in the case of pronounced brisance.

For the evaluation of the action of explosion it is necessary first of all to understand conditions and to know, what namely form of work is required from the explosion in the given case.

If work is required in the form of general action of explosion (shock waves, motion, deformation, destruction of significant volumes of medium, ejection of medium), then the basic criterion should be the total energy $Q = CQ_0$ or the total work of explosion. If work is required in the form of brisant or local action of explosion, then the basic criterion should be product $\rho_0 D^2$ or $\rho_0 D$.

Returning to criterion $Q_v \rho_0 D$, we note still another circumstance. In the derivation of the formula $\frac{Q\rho_0 D}{t}$ one proceeds from the expression for power $\frac{Q\rho_0}{l}$, i.e., the work per unit volume per unit time. The time t, entering into the expression for power, is essentially equal to the time of performance of the work. When one replaces l/D, then one thereby assumes that the time t is the propagation time of detonation over the charge. In reality, the time of accomplishment of work not equal to the time of propagation of the detonation and in general there is even no direct relationship among these quantities. The time of accomplishment of work is a variable quantity which is difficult to measure and depends not only on the properties of the explosive but also on the properties of medium, character of produced work, and conditions of explosion. The identification of this time with the time of propagation of detonation repeatedly led to serious errors. Thus, for instance, it is sometimes incorrectly assumed that if an elongated charge is initiated simultaneously at several points, thereby decreasing a few times propagation time of detonation, then the capacity should be increased a few times which should lead to corresponding increase of destructive action, including the action of shock waves. This conclusion is obviously incorrect: it is necessary, of course, only to consider that through energy redistribution local effects at points of collision of separate waves can grow.

Therefore, in general for the quantitative description of the action of an explosive one should not use the expression for power, calculated by the methods given above.

In principle, the problem of the action of an explosion near the surface of a charge could be resolved in the following way. Let us imagine the volume of medium, bordering on the charge or near surface of charge. During the explosion this volume is acted upon by a variable pressure, starting with p_{max} and then dropping rapidly (Fig. 9.3). If the character of the produced work is such that it continues to a complete drop in pressure (for instance, the case of ballistic pendulum), then in the final analysis, the action of explosion will be determined by all of the curve p(t) or in simple cases by the full impulse of the compression wave. However, in general it is necessary to consider that a given form of work (fragmentation, plastic flow) practically will cease, when the pressure has fallen to a certain value p^*, which will be attained at the instant of time t^*. For evaluating explosive action in this case it is necessary to know the course of curve p(t) in interval p_{max}-p^*, and also the boundary value p^*. Having such data for a series of points of the medium, in principle it is possible to obtain a full picture of the destroying action of the explosion, work, speeds, deformations, and destructions in various points of the medium.

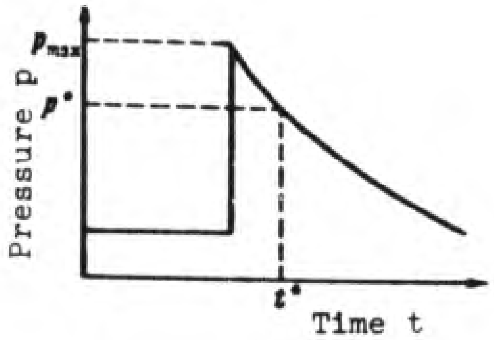

Fig. 9.3. Dependence of pressure of products of explosion on time near the charge.

Unfortunately, in practice such a method is difficult to realize. First of all, there are no simple and reliable methods of determining p(t) near the charge; it is likewise very difficult to estimate the boundary values p^*. Finally, even if curves of loads, effective at different points are obtained, the transition from loads to deformations, destructions, etc., would also be sufficiently difficult.

Summarizing the above, it may be concluded, that for a number of forms of work constituting a large part of the total work of explosion (general action), the basic determining parameter is the total energy of explosion. The density of charge for these forms of work is essential only in cases where the total energy depends on density. This takes place when the volume of charge v is given and is limited, for instance, by the body of the cartridge or the walls of the blast hole. Under these conditions, the weight of the charge is

$$C=\rho_0 v$$

and the total energy will be equal to

$$Q=CQ_0=\rho_0 vQ_0.$$

For other forms of work (brisance) directly associated with the action of products of detonation on the medium, the density of energy in the front of the detonation wave is very significant. From this follows the important conclusion that in the selection of the explosive for a definite task it is necessary to consider the conditions and character of the basic work at hand. Explosives, which are very good for one task, can be unsatisfactory for another. If it is required to produce a large general action (shock waves, ejection, expansion of "water," destruction of significant volumes of the medium), then the general energy should be great or, consequently, with an identical charge weight the specific heat of explosion should be great (more exactly, full efficiency). Certain explosives with a great specific heat of explosion can possess weak brisance. As an example it is possible to cite aluminum-containing mixtures, whose general action of which is significant (high energy of explosion), and the brisance relatively weak (due to the relatively small speed of detonation of these explosives).

If maximum brisance is required, then one should use explosives with a maximum value of the product $\rho_0 Dw \approx \frac{1}{4} \rho_0 D^2$. In this case, the pressure of detonation and density of energy in the front of the detonation wave will be maximum; the efficiency (general action) can appear moderate.

Understandably, there are explosives, which can insure and very high general action and very high brisance simultaneously.

Let us consider in conclusion of this section the diagram of energy balance in an explosion. Such a diagram is shown in Fig. 9.4 in the form of a continuous diagram. As the initial magnitude we take the potential chemical energy of explosion, i.e., that maximum energy, which is able to be released with full, the most favorable course of the explosive transformation. Due to the possibility of scattering of the unreacting explosive (see p. 372), the insufficient fullness of explosive transformation, or dissociation, the actual heat of explosion may be somewhat less than the potential by the magnitude of "chemical losses."

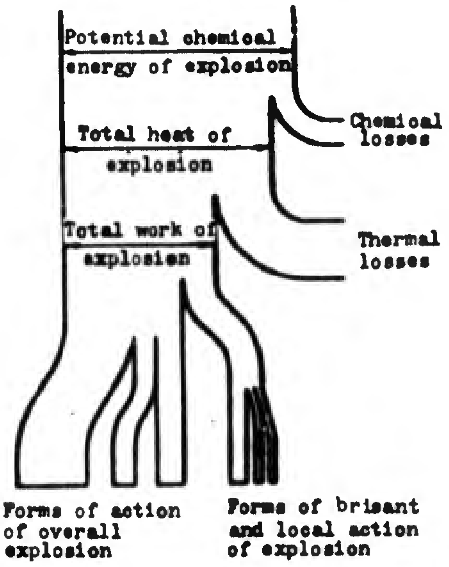

Fig. 9.4. Diagram of balance of energy in explosion.

In turn, the actual heat of explosion cannot be completely turned into work even with the ideal movement of the process of expansion. The difference between the actual heat and total work is appropriately called "thermal losses."

In Fig. 9.4, the total work is arbitrarily divided into a number of flows, representing separate forms of work of explosion. With changing of the conditions of explosion and explosive properties the separate flows can increase and decrease, disappear completely, and appear anew. As was already noted above, a large part of the total work of explosion appears in the form of general action; as regards brisance, even in the case of the most explosive materials, it constitutes the least part of the total work of explosion. Nonetheless, in certain cases it is necessary to consider the share of energy, going into brisance. If, for instance, the basic task of an explosion is the ejection or loosening of large volumes of rock, then the use of excessively high explosives (with the same total energy) can so greatly increase the energy content, going into brisance (very strong plastic flow near charge unnecessary for practical fragmentation) that the energy content, going into ejection, or loosening will increase considerably.

§ 3. Experimental Methods of Determining of Total Work of Explosion

According to the theoretical positions considered above, the work in any form of the general action of explosion is proportional to the total work of explosion

$$A_{\text{общ}}=k\cdot A_{\text{п}}.$$

[общ = gen = general]

Such a theoretical evaluation of work may be very useful; however, there is a natural desire to obtain the value of the corresponding quantity from experiment. There exist numerous experimental methods of evaluating total work, as well as individual forms of work in the general action of explosion.

In our course, we will consider the following basic methods:

a) the lead-bomb method;

b) the ballistic pendulum method;

c) the ballistic mortar method;

d) the ejection method;

e) the method, based on the measurement of pressure of the aerial shock wave.

The lead-bomb method

The lead-bomb test is the oldest method of evaluating the effeciency of explosives. It is particularly wide-spread in the Soviet Union.

The Trauzl bomb adopted as a standard at the 2nd International Congress on Applied Chemistry consists of a massive cylinder 200 mm in height and 200 mm in diameter, cast from refined lead. The bomb has on one side a hole 25 mm in diameter, lying along the axis of cylinder at a depth of 125 mm. At the bottom of the hole is placed an explosive charge (usually 10 g) with electrodetonator. The upper part of hole, not occupied by the charge, is covered with sand (Fig. 9.5a). Following the explosion of the charge, a characteristic pear-like inflation results in the bomb (Fig. 9.5b). The magnitude of this expansion in cm^3 and after subtraction of the initial volume of the cylindrical hole (61-62 cm^3) and expansion, produced by the electrodetonator, and is a measure of the relative efficiency of the explosive. For the most widespread explosives, the expansion of the lead bomb amounts to 300-500 cm^3.

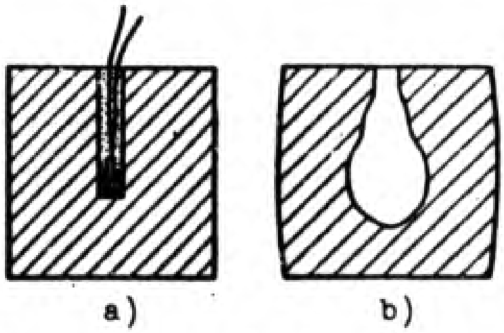

Fig. 9.5. Diagram of test in lead bomb for evaluating of explosive efficiency. a) bomb with charge, prepared for explosion, b) bomb after explosion.

This simple and widespread method of evaluating the efficiency of explosives has following fundamental deficiencies:

1. The value of the efficiency is obtained not in absolute units (kilocalories, kgm, etc.), but in certain conditional units.

2. From the magnitude of expansion it is impossible quantitatively to compare explosives directly; it is possible only to order them in a certain sequence. If, for instance, one explosive gives an expansion 250 cm^3, and the second 500 cm^3, then it is impossible to conclude that the true efficiency of second is exactly double that of the above; the charges work under dissimilar conditions with various degrees of expansion.

Let us expound briefly the method of relative evaluation of the true efficiency according to expansion in a lead bomb, as suggested by Belyayev and Kurbangalina. This method assumes the use of constant volume charges and essentially reduces to the determination of an equivalent charge of ammonite No. 6, producing the same expansion as a charge of the given substance of weight C g. This determination is carried out with the aid of graph of Fig. 9.6.

On the graph, along the axis of ordinates are laid off the weight of ammonite No. 6 charges, and along the axis of abscissas — the resulting expansion. Change of weight of charges was effected by altering density; the specific energy of explosion of ammonite No. 6 is practically independent

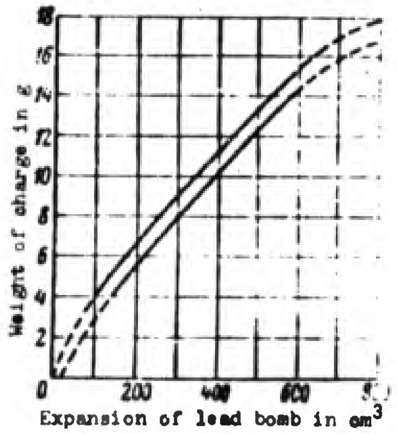

Fig. 9.6. Dependence of expansion of lead bomb on weight of charge of ammonite No. 6. Upper curve — charge taking into account equivalent weight of electrodetonator (1.1 g).

of density. The lower curve is constructed without consideration of the influence of the electrodetonator. By means of special experiments it was shown that with respect to the produced by expansion, the electrodetonator is equivalent to 1.1 g ammonite No. 6. The upper curve gives the relation between expansion and weight of charge, taking into account the effect of the electrodetonator. Thus, for instance, the standard charge of ammonite No. 6 of weight 10 g gives an expansion 390 cm^3. Considering the effect of the electrodetonator, we will find that in reality this expansion corresponds to a weight of charge of 11.1 g. A charge of 10 g without the detonator would give smaller expansion. With the standard method, the expansion, due to the electrodetonator is taken into account by subtracting 30 cm^3, which gives a value of 360 cm^3, corresponding to the standard. In reality, from a comparison of the two curves it is clear that it is necessary to subtract 45 cm^3, and the expansion, corresponding to 10 g "net" would be 345 cm^3. The correction for the effect of the electrodetonator is changed somewhat depending upon magnitude of the expansion.

Let us assume that a charge of weight C and efficiency A gives certain expansion ΔV. With help of graph of Fig. 9.6 we determine the weight of charge C_{eq} of ammonite No. 6 of efficiency A_a, giving the same expansion. If expansions are identical, then so is the work:

$$AC = A_a C_{eq}.$$

whence

$$\frac{A}{A_a} = \frac{C_{eq}}{C}.$$

This relation is a measure of the efficiency of the tested explosive.

Let us consider a concrete example. A charge of trotyl of weight 10 g (density 1.0 g/cm^3) together with the electrodetonator gives an expansion of 305 cm^3. With the aid of the lower curve (see Fig. 9.6) we find that the same expansion is given by 8.0 g of ammonite No. 6*. Thus, 10 g of trotyl are equivalent to 8 g of ammonite No. 6, whence

$$\frac{A_{\text{THT}}}{A_6} = \frac{C_{\text{[illegible]}}}{C_{\text{THT}}} = \frac{8}{10} = 0{,}8.$$

[THT = TNT]

In this case, the ratio of true efficiencies differs little from the direct ratio of the expansions (0.76-0.77). However, with significantly distinct efficiencies, the difference can be substantial.

Analogously one can determine the relative efficiency of any explosive, where the tested charge must not necessarily weigh 10 g. It is important only, that the volume of charge be constant and equal to 10 cm^3.

In Table 9.3 are given data about magnitudes of expansion in a lead bomb for standard charges (10 g) of certain explosives, as well as the corresponding values of equivalent charges of ammonite No. 6. The explosives are listed in order of increasing expansions. In this table are also given the values of the relative efficiencies according to lead-bomb tests (column 4) and the values of the relative "theoretical" total efficiencies (column 5), taken from Table 9.1. In both cases, the efficiency of ammonite No. 6 is taken to be 100.

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*Electrodetonators are identical; for this reason, the comparison may be based on the lower curve without consideration of electrodetonator action.

By comparing columns 4 and 5, it is possible to see that the coincidence of values of relative efficiencies, found by calculation with values, obtained by lead-bomb tests in most cases is good. Significant divergences are observed only for alumite No. 1 and 62% dynamite that may be easily explained.

In conclusion let us note that by means of simple calorimetric measurements, it is possible by experimental means to determine the absolute value of work, produced in the bomb. According to Belyayev and Kurbangalina, depending upon the explosive and degree of expansion, the absolute value of work, produced in the bomb, constitutes from one half to two thirds of the initial energy (heat) of explosion that will fully agree with theoretical calculations.

Table 9.3. Magnitude of Expansions for Explosion of 10 g Charges in Lead Bomb for Certain Explosives and Equivalent Charges of Ammonite No. 6

Explosive	Expansion ΔV (full, without corrections for electrodetonator) cm^3	Equivalent charge of ammonite No. 6 g	Relative efficiency according to test %	Relative total efficiency by theoretical calculation, %
1	2	3	4	5
Safety ammonite No. 8	270	7.2	72	65
Trotyl (ρ = 1.0)	305	8.0	80	81
Ammonite No. 9	350	9.0	90	93
Dynammon D	350	9.0	90	91
Ammonite No. 6	390	10.0	100	100
Tetryl	390	10.0	100	—
62% dynamite	410	10.4	104	115
Alumite No. 1	430	10.8	108	118
Hexogene (ρ = 1.0)	495	12.2	122	126
PETN	500	12.3	123	—
Simple ammonal	540	13.2	132	134

Method of ballistic pendulum

The basis of the ballistic pendulum is a suspended load, having a significant period of natural oscillations. With action on the pendulum of a flow of products of explosion or shock wave, it acquires certain momentum and deviates by a certain angle. Ballistic pendulums of various design are often used for the measurement of the impulse of products of explosion or a shock wave. A diagram of the most frequently employed design is shown in Fig. 9.7. The action of the explosion is conveyed to the face of the toe of the pendulum; the basic mass 1 is protected from the direct action of the products of explosion and shock wave by shield 5. Explosive charge 3 is detonated at some distance from the face of the toe of the pendulum, but sometimes directly at the toe.

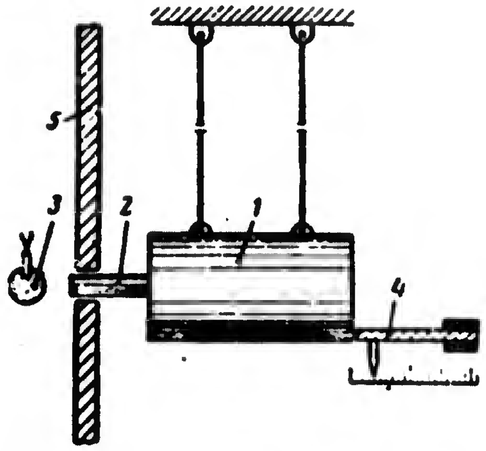

Fig. 9.7. Diagram of ballistic pendulum for determination of impulse of products of explosion or shock wave. 1) pendulum load, 2) "toe" of pendulum, 3) test explosive charge, 4) device for measurement of deflection, 5) shield.

There exists yet another design of the ballistic pendulum (Fig. 9.8). The charge is exploded in a massive mortar, the end of whose barrel lies in direct proximity to the body of the pendulum; the deflection of the pendulum is produced by the gases of explosion, emerging from the mortar barrel; (this device should not be confused with the ballistic mortar, which will be described below).

In the testing of a given explosive, one commonly determines the charge which gives the same deflection as a 200 g charge of a certain standard explosive. The merit of method lies in the fact that charges of considerable weight (near 200 g) can be tested.

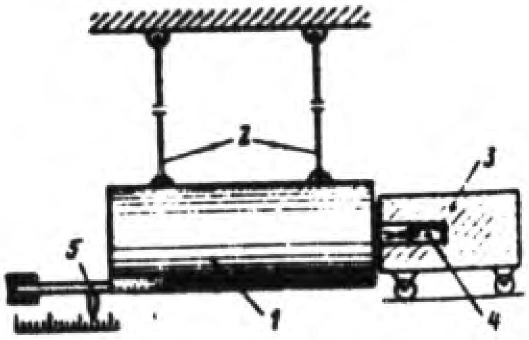

Fig. 9.8. Diagram of ballistic pendulum for determinaton of relative efficiency. 1) pendulum load, 2) suspensions, 3) mortar, 4) explosive charge, 5) device for measurement of deflections.

However, a pendulum of this type does not allow the estimation of absolute values of work, and even relative values may differ from true ones due to the complexity of conditions, and small and indefinite degrees of expansion of products of explosion.

Let us return to pendulum, a diagram of which is shown in Fig. 9.7. If the pendulum under the action of an explosion deviates by an angle φ, then the magnitude of impulse, conveyed to the toe of pendulum, will be equal to

$$J = M\sqrt{2gl(1-\cos\varphi)}, \quad (9.30)$$

where M is the mass of pendulum,

l is the length of suspension,

g is the acceleration due to gravity.

Formula is valid for angles φ not more than 15-20°. Instead of measuring angle φ it is possible to measure the horizontal displacement of the pendulum x. It is possible to show easily that for small angles, the impulse will be given by the relationship

$$J = M\frac{2\pi}{T}x, \quad (9.31)$$

where T is the period of oscillations of the pendulum.

From the values of the impulses, it is possible in principle to obtain values of energy on the basis of the known relationship between the energy of motion and magnitude of impulse:

$$E = Mgh = \frac{J^2}{2M}, \quad (9.32)$$

where h is the height of rise of pendulum.

On the basis of expression (9.32), it is possible to estimate the energy conveyed to the toe of the pendulum, and hence to calculate the total shock wave energy. Unfortunately, the practical use of this method requires surmounting of many difficulties; in particular, it is necessary to definitize considerably the question of the reflection impulse and the impulse of the forward-moving shock wave.

Ballistic mortar method

The ballistic mortar (Fig. 9.9) is a variant of the ballistic pendulum; its design is especially adapted to the determination of efficiency. The massive body of the mortar is suspended on cables in the manner of a pendulum. In the body is an explosive chamber of volume v_{exp}, in which the charge is detonated, and an "expansion" chamber of volume v_{expa}, in which before detonation is placed a massive steel piston-missile. During detonation of charge (usually of weight 10 g) the gases in the beginning, producing practically no work, occupy the volume of the detonation chamber. Their pressure is essentially lowered; their internal energy and temperature, as we have seen, can be considered practically constant. The work of explosion in the ballistic mortar consists in the ejection of the piston-missile. When the missile departs (i.e., when its rear face passes the butt end of the mortar), the gases of explosion will escape into the air, and

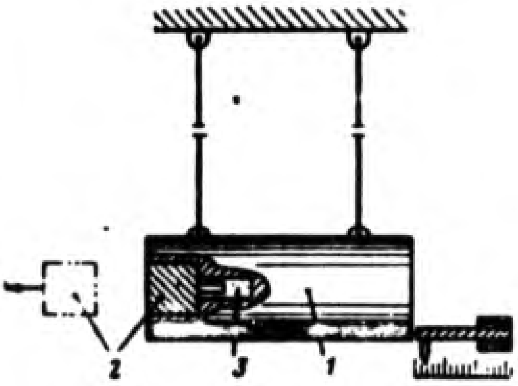

Fig. 9.9. Diagram of ballistic mortar for determination of absolute efficiency. 1) mortar body; 2) piston-missile; 3) explosion chamber with explosive charge.

the work in the mortar-missile system will cease.

Special measurements indicated that from the moment of explosion of departure of missile there elapse 5-10 milliseconds; this time is comparatively great; it is in any case 20-30 times longer than the time of expansion of products of explosion of the charge (weight 10 g) in air up to atmospheric pressure.

The magnitude of work, performed in the mortar, will be given by the formula

$$A_{\text{м}} \approx E\left[1-\left(\frac{v_{\text{взр}}}{v_{\text{взр}}+v_{\text{расш}}}\right)^{k-1}\right] \qquad (9.33)$$

[М = mo = mortar; взр = exp = explosion;
расш = expa = expansion]

On the other hand, the value A_{mo} may be determined from experiments with mortar deflection.

The total mechanical energy E_{mo}, obtained in the explosion in the mortar-missile system, is equal to

$$E_{\text{м}} = E'_{\text{м}} + E_{\text{с}} = E'_{\text{м}}\left(1+\frac{E_{\text{с}}}{E'_{\text{м}}}\right) \qquad (9.34)$$

[с = mi = missile]

where E'_{mo} is the kinetic energy of the mortar proper;

E_{mi} is the energy of the missile.

Furthermore,

$$E'_{\text{м}} = \frac{1}{2}J\omega^2, \qquad (9.35)$$

where J is the moment of inertia of pendulum;

ω is the angular velocity of the pendulum.

In turn,

$$E_{\text{с}}=\frac{1}{2}mu^2, \qquad (9.36)$$

where m is the mass of the missile; u is the velocity of the missile.

To determine by experimental means mechanical energy E'_{mo} easier than the energy of the missile E_{mi}; therefore, let us eliminate E_{mi}, taking into account that the angular momenta of the mortar and missile have to be equal,

$$J\omega=mur, \qquad (9.37)$$

where r is distance of the axis of the detonation chamber from the point of suspension.

Usually the mortar is designed in such a way that the axis of the detonation chamber passes through the center of gravity of the pendulum. Then r = l, where l is the distance from center of gravity to point of suspension.

From expressions (9.35)-(9.37) we obtain

$$\frac{E_{\text{с}}}{E'_{\text{м}}}=\frac{J}{mr^2},$$

or

$$E_{\text{м}}=E'_{\text{м}}\left(1+\frac{J}{mr^2}\right). \qquad (9.38)$$

It is evident that

$$E'_{\text{м}}=Mgh, \qquad (9.39)$$

where h is the elevation of the center of gravity of the mortar.

If φ is the angle of deviation, then

$$h=l(1-\cos\varphi); \qquad (9.40)$$

$$E'_{\text{м}}=Mgl(1-\cos\varphi). \qquad (9.40a)$$

Consequently, the total energy of system is

$$E_{\text{и}}=Mgl\left(1+\frac{J}{mr^2}\right)(1-\cos\varphi).$$

Denoting

$$E_0=Mgl\left(1+\frac{J}{mr^2}\right),$$

we finally obtain

$$A_{\text{и}}=E_{\text{и}}=E_0(1-\cos\varphi). \qquad (9.41)$$

For a mortar of given design the quantity E_0 is a constant parameter.

Thus, with the aid of a ballistic mortar one can determine absolute value of work of explosion. Comparing the obtained value with the theoretical one [formula (9.33)], it is possible to definitize the separate parameters of the theoretical formula, for instance quantity k.

If the volume of the detonation chamber is sufficiently great and there is a device for receiving the missile (box containing clay), the ballistic mortar, not being destroyed, can sustain hundreds of explosions. With strict constancy of conditions, separate experiments in the mortar give scattering of results of less than 1%.

Unfortunately, experience in the application of the ballistic mortar shows that the real character of work of the explosion in the mortar apparently differs from the ideal. Let us enumerate certain "hidden" deficiencies of mortars which lower its value as an instrument for determining the absolute work of explosion.

1. The volume of the explosive chamber of the mortar usually is sufficiently large (with respect to weight of charge); otherwise

the chamber would be quickly destroyed. Therefore, the expansion ratio $\frac{v_{exp} + v_{expa}}{v_{exp}}$ is small (usually less than in a lead bomb); the pressure even in the initial stage is relatively small.

2. With changes in the location of the charge in the chamber (other conditions being constant), the amount of deviation of the pendulum changes somewhat.

3. Aluminum-bearing explosives (and also, probably, other explosives with similar properties) give under the conditions of the mortar an evidently decreased value of work; this is possible to explain on the basis of the general hypotheses regarding the work of explosion, taking into account that the expansion ratio in the mortar is relatively small. Thus, in a ballistic mortar with an expansion ratio

$$\frac{v_{\text{взр}} + v_{\text{расш}}}{v_{\text{взр}}} \approx 8{,}25$$

it was found that the efficiency of elementary ammonal (mixture of powered aluminum and ammonium nitrate) under the conditions of the mortar is equal to 334 kcal/kg, while the efficiency of ammonite No. 6 is 310 kcal/kg. Thus, according to mortar tests the efficiency of ammonal is only 1.08 times higher than the efficiency of ammonite No. 6. At the same time, the ratio of energies of explosion is equal to 1.53 and the ratio of the computed total efficiency (with expansion to atmospheric pressure) is near 1.34.

The apparent divergence of experimental and calculated values is easy to explain, With low expansion, the relative efficiency of ammonal, possessing the low value k, is significantly lowered (this circumstance may be seen directly from the graph of Fig. 9.1; the smaller the expansion ratio, the larger the relative distinction of values A_t/Q for various k). If one were to calculate the theoretical ratio of the efficiencies of ammonal and ammonite No. 6 for a degree of expansion 8.25, taking into account the distinction of indices of the adiabatic then it will appear equal to ~1.10, i.e., will practically coincide with the experimental value. Thus, the small indices of ammonal during tests in the ballistic mortar are simply explained by the small expansion ratio of gases of explosion; it is therefore incorrect to explain the relatively small work of ammonal in the mortar by the slow burning of aluminum (and such attempts are sometimes made). If the data obtained for ammonal during tests in the mortar are extrapolated for large expansions (in particular, for expansions to atmospheric pressure), then one obtains a value which corresponds to the efficiency calculated on the basis of the general hypotheses. It is clear that the necessity of such extrapolation reduces the value of the ballistic mortar method.

Thus, although the ballistic mortar is theoretically an ideal instrument for the measurement of the work of an explosion, its practical use is hampered by the indicated circumstances.

Appraisal of efficiency according to ejection funnel

The size of the funnel, formed by an explosion in the ground, directly determines that form of work, which was called the high-explosive action. Above (see p. 663) it was shown that the volume of the ejection funnel depends on the weight and location of the charge, the properties of the explosive and on the properties of the medium.

The weight of the charge $C = Kvf(n)$, where K depends on the properties of the medium, as well as on the properties of the explosive (v is the volume of ejection). The value of K in formulas (9.20) or

(9.22), obviously, constitutes the specific expenditure of the explosive, i.e., the expenditure of the explosive per unit volume of the ejected rock, reduced to n = 1. If explosions are produced with observance of similarity and with constancy of the properties of the ground, then the change in the specific expenditure maybe only by a change of the efficiency of the explosive. Therefore, in that case where for one explosive we obtain a value K_1, and for the other K_2, then, tentatively, the ratio of their efficiencies is $A_1/A_2 = K_2/K_1$. Comparisons must be made with maximally close values of n.

The method of funnels is valuable by virtue of the fact that it allows the testing of charges of significant weight under conditions of practical use.

The deficiencies of the method consist in poor recurrence and low accuracy. In the performance of experiments, the properties of ground even in neighboring sections can differ somewhat; changes in humidity and other difficult-considered factors are essential. The volume of ejected ground is usually determined by the measurement of the linear dimensions of the funnel, and inasmuch as the volume is proportional to the cube of the linear dimensions a small error in their measurement can give a significant error in the evaluation of the volume. Since the errors of individual experiments may be significant, it is necessary to conduct a large number of experiments whose performance is more complicated than are laboratory tests. Therefore, the method of funnels is essentially a final field test; it must be preceded by preliminary experiments with use of the lead bomb or another laboratory method.

Method of evaluation of efficiency according to air shock wave

This method is based on the measurement of the excess pressure

Δp_1, at the front of the shock wave and the determination of the trotyl equivalent according to the law of similarity. In Chapter VI it was shown that for trotyl there is a fixed simple dependence between the excess pressure and the reduced distance $\Delta p_1 = f(\overline{R})$. The form of function f is known. Let us assume that we took a charge of weight C with an unknown efficiency A_x. Let us assume further that at a distance R we measured the pressure on the wave front, equal to $\Delta p_1'$. With the use of trotyl, this pressure $\Delta p_1'$ at the same distance R would be attained at the reduced distance

$$\overline{R} = \frac{R}{\sqrt[3]{C_{THT}}},$$

whence

$$C_{THT} = \left(\frac{R}{\overline{R}}\right)^3.$$

Having thus determined the charge of trotyl, which gives the same $\Delta p_1'$ that the test charge of weight C, we can determine efficiency of the charge:

$$A_x = A_{THT}\frac{C_{THT}}{C}. \qquad (9.42)$$

The advantage of this method, just as of the method of funnels, is the possibility of the use of very big charges. The deficiencies method consist in the necessity very exactly measuring Δp_1: the small error, admitted in the measurement of Δp_1, can give a substantial error in the evaluation of C_{eq}. Furthermore, with the explosion in air of small charges of substitute explosive with a low rate of chemical transformation, it is necessary to intorduce a correction for the scattering of the explosive.

It is possible to note that the described method of evaluating the relative efficiency with an air shock wave is still not a standard and widespread method, but its use is becoming ever wider.

All the described methods of evaluating the overall action of an explosion permit estimation of the efficiency of the explosive, even if what is measured is only a particular form of the overall action of the explosion (as, for instance, in the method of ejection). With given constant conditions and the observance of similarity, the amount of work in a given particular form constitutes definite share of the total work. The resulting values of relative efficiency can be used to evaluate total efficiency.

§ 4. Experimental Methods of Evaluating Explosive and Local Action of Explosions

1. Evaluation of Impulse of Local Action of Explosion

The best method of evaluating the local action is the method of ballistic pendulum. With this method, the charge whose local action is to be evaluated, is placed directly on the toe of the ballistic pendulum as shown on Fig. 9.10. The experimental value of the impulse of the local action of the explosion is calculated by measuring the deflection using formulas (9.30) and (9.31).

As a result of extensive research, P. F. Pokhil and M. A. Sadovskiy established a connection between the value of the impulse, fixed according to the deflection of the pendulum and the basic characteristics of the charge, and proposed the above formula (9.29) for the evaluation of the impulse of the local action

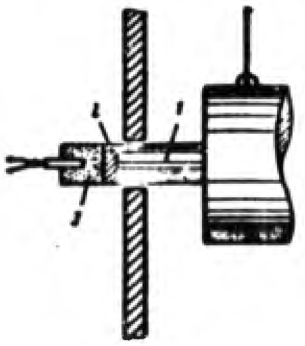

Fig. 9.10. Diagram of ballistic pendulum for evaluating the local action of an explosion. 1) toe of pendulum, 2) steel plate, 3) explosive charge.

of explosion.

From this formula it follows that for obtaining maximum local action with open-standing charges, the quantity S_c/S_t – the ratio of the charge surface, adjacent to destroyed object to the total charge surface – should be as large as possible. For obtaining the maximum local action of an open-standing charge it is appropriate, in particular, to give it one of the forms depicted in Fig. 9.11.

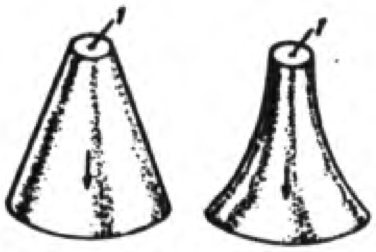

Fig. 9.11. Form of charges, insuring increased local action of explosion in direction, indicated by arrow. 1) point of initiation.

2. Appraisal of Brisance of Explosion

The simplest and most widespread method of the test for brisance is the test employing compression of lead columns, or the Hess test (see All-Union State Standard 5984-51).

For the test we employ a lead column 60 mm in height and 40 mm in diameter. On the column we place a steel plate by 10 mm in thickness and 41 mm in diameter. On the steel plate we place the charge. In standard tests, the weight of the charge constitutes 50 g, the weighed charge is loaded in a paper cylindrical cartridge 40 mm in diameter usually the pressing is produced by a load of 1 kg for 2 min. For various explosives, somewhat different densities are obtained. It is more correct to press the charge to constant density, for instance $\rho_0 = 1.0$. Simultaneously with pressing a 15-mm deep hole is formed for the detonator capsule. For centering the detonator capsule a cardboard circle with a hole is usually placed over the explosive. Lead column with plate and charge is placed on a massive steel support.

In Fig. 9.12 is shown a diagram of the whole device, prepared for detonation. Upon explosion, the lead column is deformed, assuming a

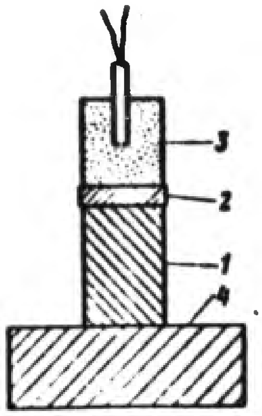

Fig. 9.12. Diagram of preparation of experiment for the evaluation of brisance by compression of lead column (Hess test). 1) lead cylinder, 2) steel plate, 3) explosive charge with electrodetonator, 4) steel support.

Table 9.4. Results of Hess Tests

Explosive	Compression in mm
Tetryl	20-22
Trotyl	16
Ammonite No. 6	14-15
Ammonite No. 9	11-13
Dynammons	10-12

characteristic mushroom-like form (Fig. 9.13).

The measure of the brisance is the depression of the column, i.e., the difference between its average heights before and after explosion, expressed in mm. With standard tests, the Hess test gives the data in Table 9.4.

It is necessary to note that the compression of the column, especially in the case of ammonite and dynammon, strongly depends on the degree of crushing of components of the explosive. With very thorough crushing of the dynammon it is possible to obtain compression on the order of 15-17 mm; on the other hand, coarsely crushed dynammon gives much lower compression. The exceptional simplicity of the Hess test determines its use in testing mixtures, especially industrial explosives upon receipt. Ammonite No. 6 (see Table 9.4) should have a brisance by the Hess test of 14-15 mm. Let us assume that, in testing ammonite from a certain lot we obtained a brisance of 10 mm. It is obvious that the given lot does not correspond to the standard. This lot was either prepared with inferior properties (for instance, due

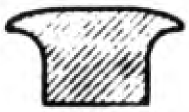

Fig. 9.13. Shape of lead column, compressed by explosion.

to insufficient crushing and mixing), or deteriorated in its explosive properties during storage (moistening, caking).

The Hess test, being indispensable as an approval test, has essential deficiencies as a method of appraisal of brisance. Basic among them are the following.

1. The final result is obtained not in units of energy or work, e.g., work of deformation of a lead column, but rather in units of length. It is important to emphasize that with compression, the resistance of the lead column increases and therefore the compression (shrinkage) column is combined nonlinearly with the magnitude of work of deformation. If compression doubles, (for instance, becomes 20 mm instead of 10 mm), then the work of compression increases not less than three times.

2. Compression under conditions of the Hess test is sometimes in significant measure determined by the detonational ability of the explosive; and the magnitude of its critical diameter.

Let us compare, for instance, hexogene and some industrial ammonite. We will denote the maximum rate of detonation, attainable by a given explosive at a given density by D^*. In the comparison of hexogene and ammonite, the latter should give high compression already by virtue of the fact that $D^*_{hex} > D^*_{am}$. However, under the conditions of the Hess test, the difference obtained will be still greater. The fact is that the critical diameter of hexogene is very small (1-2 mm) and therefore charge 40 mm in diameter detonates at a rate, equal to the maximum $D_{hex} = D^*_{hex}$.

The critical diameter of ammonite, depending on composition and the degree of crushing may be equal to 10-20 mm, therefore, for charge 40 mm in diameter, the speed of detonation of ammonite will be less than the maximum $D_{am} < D^{*}_{am}$; furthermore, the ammonite will have a significant section "acceleration" of detonation. Therefore, the comparison of the effects of open-standing charges of hexogene and ammonite 40 mm in diameter can give an incorrect conception of effects under other conditions. Thus, for instance, under blast hole conditions the speed of detonation of hexogene will remain practically the same, and the speed of detonation of ammonite can increase essentially. Certainly, under blast hole conditions as well, hexogene will give a larger explosive effect than ammonite, but difference between them will be less than is obtained with comparison of open-standing charges.

3. The use of the standard Hess test is possible only for low brisances. If one were to take powerful, full-strength explosives (PETN, hexogene etc.), then application of the test becomes difficult even $\rho = 1.0$ and becomes absolutely impossible at significant densities, i.e., precisely at those densities, at which brisance appears with the greatest intensity and is of especially great interest. The fact is that with significant brisance, steel plate is destroyed, which in turn leads to the strongest destruction of the lead column turning it into a ripped, shapeless mass. In order to avoid this, sometimes thicker plate (20 mm) or two standard plates are used, or instead of the standard charge 50 g in weight a 25 g charge is taken. The compressions, naturally, are significantly less.

Let us consider in brief certain questions, involved in the theory and conditions of work of the Hess test lead column. Pokhilom and Sadovskiy showed that the real work of deformation of a lead column may be approximated by the quantity

$$\varepsilon = \frac{\Delta h}{h_0 - \Delta h} = \frac{\Delta h}{h_k}, \qquad (9.43)$$

where Δh is the compression of the column;

h_0 is the initial height;

h_c is the final height of the lead column.

Function α increases faster than Δh, and takes into account the increase in the resistance of the column with compression. The use of quantity α as index of the "true" brisance is more justifiable than its direct evaluation by the value of compression Δh.

Let us note that externally, the same form of work, i.e., plastic flow of lead under the conditions of the Trauzl bomb, is the characteristic of efficiency, the characteristic of general action; while under the conditions of the Hess test, plastic flow is the characteristic of brisance.

Sometimes in the case of explosives with low detonational capability, which fail under the conditions of the Hess test, the charge is placed in a steel shell. In the presence of such a shell, the value of compression determines something intermediate between general and brisance action. In the limiting case, if one were to place charge in very massive shell, i.e., under conditions, where there is no emergence of products into the air and a large part of the total work of explosion is released in the system, the magnitude of compression of the lead column will increase sharply and will be determined by the efficiency of the charge.

Recently, the deformation of lead columns has frequently been used for characterizing detonational ability, characterizing the power of the initiating impulse etc.; this involves working with charges, significantly longer than standard charges used in the Hess test. Even if the charge is incapable of stable detonation, then a powerful initiator is able to "run" the damped detonation over a larger distance, which is very conveniently and simply fixed according to compression of the column.

Fig. 9.14 shows a diagram of another method of determining brisance with the aid of the Kast brisantometer.

The action of the explosion of the charge is transmitted through a relatively massive steel piston to a copper crusher, producing its deformation; the magnitude of compression of the crusher is the characteristic of brisance. Thus, as under the conditions of the Hess test; as crusher compression rises its resistance increases. Therefore, with increasing compression, the "true" brisance increases faster than actual compression.

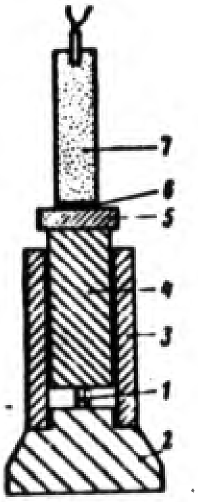

Fig. 9.14. Diagram of preparation of experiment for evaluating brisance by means of the Kast test. 1) copper crusher, 2) support, 3) guide bushing, 4) cylindrical piston, 5) steel plate, 6) lead plate, 7) explosive charge.

Tests are carried out with charges of constant volume 21 mm in diameter and 80 mm in height. With the help of the Kast brisantometer, it is possible to measure the brisance of powerful, high-density explosives.

Certain other methods are also used in evaluating brisance. Of these, we may note the shell splitting test. An explosive charge in a shell (e.g., in the body of an artillery shell) is detonated in a sand pit. After detonation fragments are gathered and sorted out by weight. The more intense the fragmentation, the greater the total weight of the small fragments, and the more explosive the explosive charge. It is necessary to note that the degree of splitting depends essentially on the material of shell, therefore, if it is intended to use the tests for evaluating the properties of the charge, then the test must be conducted with shells of strictly constant properties.

An evaluation of the fragmentation action may also be obtained from data about the size of dents in plates, from data on the piercing of steel plates, etc. Under the condition of standardization of volumes of charges, and also of the properties and dimensions of the plates utilized these methods, being essentially strictly qualitative, undoubtedly, can provide certain tentative data for the quantitative appraisal of the fragmentation action of the explosive.

§ 5. Cumulative Action of Explosions

Above we considered usual forms of work, arising during the explosion of practically any charge. There are, however, specific forms of the work of explosion, obtained in the detonation of charges of special arrangement. As an example let us consider the so-called action (from Latin work cumulatio – to increase, to summarize, to accumulate). The essence of the phenomenon consists in increasing the action of explosion of a charge in definite direction.

In Chapter VI we showed that near the charge, the action of explosion depends on the form of the charge. Thus, in the case of charge of cubic shape, in the directions of the sides of the cube, the action is significantly stronger than in the directions of the angles. Already in this example we encounter directed explosive action, produced by the fact that the products of explosion in the initial stage move perpendicularly to the surfaces of charge. In cumulative action, the effect of directivity of the explosion appears especially strongly and clearly.

Fig. 9.15a shows a charge in the shows a charge in the shape of

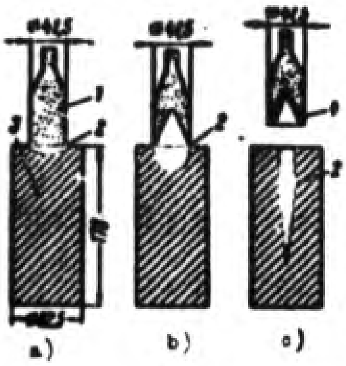

Fig. 9.15. Action of solid charge on steel support of (a), a charge with cumulative recession (b), and a charge with a cumulative recession in the presence of facing (c). 1) charge, 2) hole in steel support, produced by explosion, 3) steel support, 4) metallic facing.

a bottle, set on a steel cylinder. The figure is executed in scale, and the basic dimensions are shown in mm. The explosive used was pentolite (alloy of trotyl and PETN); the weight of the charge was 150 g. After the explosion (initiation produced from above), the steel exhibited a depression, shown in Fig. 9.15a (in section) as a blacked-out area.

On a similar steel cylinder was detonated a charge, having conical recession, oriented toward the surface of the steel (Fig. 9.15b). The external dimensions of the charge were as before, but the weight of it decreased to 115 g. One would think that the action of such a charge would be weaker than that of a solid charge; the weight of charge is less; moreover, precisely that part of charge is removed which directly adjoins the steel cylinder and in the case of the explosion of a solid charge is most active. In reality, the action of a charge with a recession turns out to be more intense, as may be seen from the dent (blacked out region in Fig. 9.15b). After the explosion of a charge with a conical recession, the depth of the resulting dent is approximately 4 times larger than from the solid charge. Such intensification of the action of explosion in given direction, produced by a charge of definite form, is called cumulative action, and the corresponding charges — shaped charges. Sometimes the term "cumulative action" applies also to effects, produced by a combination of several charges.

Cumulative action has the strongest effect, if on internal surface of the conical recession is placed a film of metal. On Fig. 9.15c is shown result of an analogous experiment with a charge, whose cumulative recession is faced by steel of a thickness 0.6 mm. The hole in the steel (shown in figure as black region) has a somewhat smaller diameter, but its depth is approximately 4 times greater than the depth of the recession due to the shaped charge without facing and, consequently, approximately in 16 times greater than the depth of dent, produced by the solid charge. It is necessary to note that the greatest depth, in case of a charge with facing, is obtained, when it is located not on the actual surface of the pierced target, but at a small distance, as was shown on Fig. 9.15c.

Shaped charges with metallic facing have exceptionally great practical value, so that both in experimental, and in theoretical studies of the cumulation phenomenon, attention was centered on these charges.

Fig. 9.16 shows consecutive stages in the process of compression by a detonation wave of the metallic facing of conical cumulative recession. The detonation wave spreads from left to right. Under the action of the pressure of the detonation wave, the facing starts to move to the center, as if being compressed and converging. After convergence, the substance of the facing is divided into two parts, whose role is essentially different. To the left from point of convergence ("node"), the external layers of the facing will form "pestle" (or rod), 2, into which the larger part of the mass of facing passes. The pestle (rod) does not play any role in the piercing action. On the

Fig. 9.16. Consecutive stages in the formation of the cumulative stream. 1) position of detonation front, 2) pestle, 3) stream.

right of the point of closing, the internal layers of the facing will form cumulative stream 3, a stream of metal moving with great speed toward the right. Precisely this stream, in spite of the fact that its mass is small, assures the piercing of barriers of significant thickness.

Fig. 9.16a, b, c and d, from left to right, is shown schematically the process of stream and pestle formation with the propagation of detonation. In Fig. 9.16a, the detonation wave had begun to compress the apex of the cone; in Fig. 9.16c, the detonation wave has passed the end of the charge; Fig. 9.16d shows the subsequent development of the phenomenon a certain time after the detonation wave has passed the end of the charge. Such consecutive photographs of process of formation of the cumulative stream can be obtained (and repeatedly have been obtained) with the aid of pulse X-ray photography, i.e., with an instrument, giving powerful but very brief pulse of x-radiation. If the studied object is placed between the X-ray tube and a photographic plate, then on plate will be recorded the instantaneous distribution of masses.

By conducting several detonations of completely similar objects, photographed at various instants (from the start of the explosion), it is possible to obtain a full picture of the development of the phenomenon in time. Pulse X-ray photography is very effective in the study of such phenomena as, for example, the bursting of a shell and the initial stage of scattering of fragments, and is especially effective in research on the cumulation phenomenon. Optical methods were also used, but in this case their usefulness is limited.

Let us turn to the theory of phenomenon. There exists a hydrodynamic theory of shaped charges with facing, which considers the facing material as an ideal incompressible liquid. For the first time, the solution of problem was given by M. A. Lavrent'yev; it is the most vigorous solution. Somewhat later, questions of cumulation theory were considered less vigorously by a number of US researchers. We will expound in brief certain basic positions and conclusions of the hydrodynamic theory of cumulation. On Fig. 9.17a is shown a section of shaped charge with metallic facing. From this section may be obtained wedge-shaped charge by parallel translation of the perpendicular axis of symmetry or conical by means of rotation of the section around axis of symmetry. Further conclusions, strictly speaking, will pertain to a wedge-shaped charge. It is possible to apply them to a conical charge only under the condition that the thickness of the conical facing decreases from summit of cone to base in such a way that the mass of the shell per unit of length (along the axis of symmetry) remains constant. However, with a certain error, conclusions presented below can be applied to conical charges with a constant thickness of the layer of conical facing. An important characteristic of the facing is the angle α between the side of wedge (generatrix of cone) and axis of symmetry.

Fig. 9.17b schematically shows the process of destruction of shaped charge facing. We consider the elementary case of a flat detonation wave. Under the action of this wave, the facing starts to move to the center; the angle 2β between the moving walls will be larger than the initial angle 2α between the walls of the shell. On the left of the "node" (point 0 of convergence of walls) is a pestle, formed from the external parts of the facing. On the right is the cumulative stream, formed from the internal parts of facing. With the compression of the facing, the "node" (point 0) will move with a certain velocity

u_n from left to right, i.e., in the direction of propagation of the detonation. If we introduce a movable system of coordinates rigidly connected with the "node," then in this system the material of the shell will, as it were, flow into the node with a certain velocity u' and with the same velocity to flow out of the node to the right – into the stream and to the left – into the pestle.

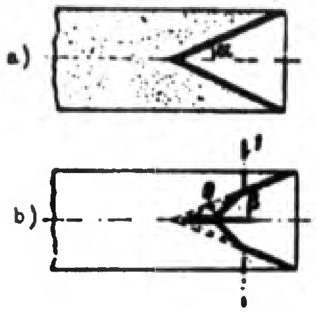

Fig. 9.17. Diagram of shaped charge (a) and formation of stream (b). 1) position detonation front.

With respect to a stationary system of coordinates the velocity of the stream is $u_s = u_n + u'$; the velocity of the pestle will be different; if in a movable system of coordinates it moves to the left, then with respect to the stationary system, it will move to the right, but with a speed, significantly smaller than the speed of the stream $u_p = u_n - u'$. Considering the material to be incompressible and applying the Bernoulli equation, we obtain the following relationships:

$$u_c = D\frac{\sin(\beta-\alpha)}{\cos\alpha}\left(\frac{1}{\sin\beta}+\frac{1}{\operatorname{tg}\beta}+\operatorname{tg}\frac{\beta-\alpha}{2}\right); \tag{9.44}$$

[c = s = stream]

$$u_п = D\frac{\sin(\beta-\alpha)}{\cos\alpha}\left(\frac{1}{\sin\beta}-\frac{1}{\operatorname{tg}\beta}-\operatorname{tg}\frac{\beta-\alpha}{2}\right). \tag{9.45}$$

[п = p = pestle]

where D is the speed of detonation of the explosive.

If m is the mass of the facing material, then the mass of substances, forming the stream and pestle, respectively, are determined by the following expressions:

$$m_c = \frac{m}{2}(1-\cos\beta); \tag{9.46}$$

$$m_п = \frac{m}{2}(1+\cos\beta). \tag{9.47}$$

From these relations it follows that the mass of the stream is less than the mass of the pestle, but possesses significantly greater velocity; as a result, the piercing action is determined precisely by the stream. The smaller angle α, the greater the velocity of the stream. For a cone (wedge) with $\alpha = 30^{\circ}$, the velocity of the cumulative stream should be close to the velocity of detonation and even somewhat in excess of it.

If $\alpha \rightarrow 0$, then $v_s \rightarrow 2D$. Thus, maximum theoretical velocity of the stream in limit is equal to double the velocity of detonation. If an explosive with a sufficiently high speed of detonation (7.5-8.5 km/sec) is used, then speed of the stream will be high as well. As a result of collision with the barrier of such a stream, possessing moreover significant density a pressure of hundreds of thousands of atmospheres is developed. With such pressures, even durable metals should leak, which justifies the application of hydrodynamic equations to the metal in the stream.

From the theory it also follows that length of stream l_s, length of the pestle l_p (rod), and length of generatrix of the wedge (cone) l have to be equal to each other.

It is necessary to note that the derived relationships give correct qualitative dependences, but quantitatively are undoubtedly approximate. Experimental research shows that the real distribution of the mass of facing in pestle and stream differs somewhat from that given by the above approximate theory. The same can be said of the velocities and first of all of the velocity of the stream. It turned out that the head of the stream moves with a higher velocity than its tail portion. Therefore, in the course of movement, the stream is stretched and its length increases. Furthermore, the stream can be still pressed out after full closing of the walls due to extremely high pressures developed in axial part of the pestle. Therefore, the theoretical relationship $l_s = l_p = l$, even if valid, holds only at the stream; subsequently, during its motion $l_s > l$. Above we considered the diagram for the elementary theory. At present, there are well-developed, refined variants of the theory.

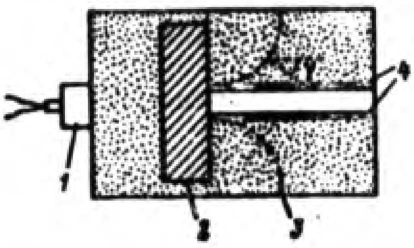

Fig. 9.18. Diagram of shaped charge with cylindrical recession and facing. 1) detonator, 2) screen of inert material, 3) front of detonation wave at some intermediate instant, 4) facing.

Let us consider an interesting case of a shaped charge, a section of which is shown schematically in Fig. 9.18. In this case, the cavity constitutes a cylinder and the angle $\alpha = 0$. Furthermore, in the way of propagation of the detonation is massive steel plate (screen), around which the detonation wave curves. As a result, the propagation of the detonation wave will occur under certain variable angle γ to the direction of propagation of the plane wave. (The wave with $\gamma = 0$ is flat and glides along the facing; the wave with $\gamma = 90^\circ$ is incident on the facing normally.) As we already saw with $\alpha = 0$ and $\gamma = 0$

$$u_c = 2D.$$

If $\gamma \neq 0$, then

$$u_c = \frac{2D}{\cos\gamma}.$$

Finally, if $\gamma \to 90^\circ$, then $u_s \to \infty$.

It is necessary, however, to recall that with $\gamma \to 90^\circ$ and simultaneously $\beta \to 0$, and conseauently $m_s \to 0$ as well.

With the arrangement shown in Fig. 9.18, the angle of propagation of the detonation wave γ is variable. Near the shielding plate γ is close to 90°, but then decreases.

Studying shaped charges of the type of shell, shown in Fig. 9.18, US researchers measured the speed of the stream for facing made of various materials. These speeds turned out to be the greater, the less the atomic weight of the facing material. For facing made of beryllium a record value of stream velocity 90 km/sec was obtained. It is necessary, however, to note that such a velocity is obtainable for a stream, propagating in a vacuum. Besides, the mass and density of streams are minute, and the piercing action of the stream insignificant; if vacuum worsens and the pressure attains just 0.1 mm Hg, then the stream already noticeably slowed down. From certain theoretical relationships, it follows that the pressure on the axis of the cylindrical recession (during its compression and formation of the cumulative stream) can attain several million atmospheres.

Heretofore, we have considered the formation of a cumulative stream and its parameters. We will turn now to the interaction of stream with the barrier. Encountering the barrier, the cumulative stream deforms it; the material of the barrier starts to spread in radial directions, forming a hole, which deepens at a certain rate. Once again, due to the very high velocities of motion of the stream, its interaction with the barrier can be considered as the interaction of ideal liquids, applying to them equation of hydrodynamics as was proposed by Lavrent'yev.

Let us assume that we have cumulative stream of density ρ_s, length l_s, moving with velocity u_s. On Fig. 9.19 we see the penetration of stream into the barrier. Point A (point of "impact") shifts deeper inside with a certain speed u_{ma} until stream is spent. The

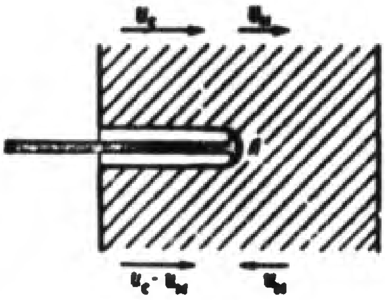

Fig. 9.17. Diagram of penetration of barrier by a cumulative stream.

arrows above show the true values of the velocities.

Let us now turn to the coordinate system moving together with point A. With respect to this system of coordinates, the material of the barrier will move to the left with velocity u_{ma}, and the stream — to the right with velocity $u_s - u_{ma}$. These velocities are shown by arrows on the figure below. For a moving coordinate system we have stable motion and are able, considering the liquid by incompressible, to apply Bernoulli equation ($p + pu^2/2 = \text{const}$). Setting the pressure p from both sides of surface of contact of the stream and barrier (at point A) identical, we obtain

$$\rho_c(u_c - u_м)^2 = \rho_м u_м^2,$$

[м = ma = material]

whence

$$\frac{u_м}{u_c - u_м} = \sqrt{\frac{\rho_c}{\rho_м}}. \tag{9.48}$$

The depth of full penetration (depth of piercing) is

$$L = u_м t,$$

where t is the time of action of stream, equal to

$$t = \frac{l_c}{u_c - u_м},$$

so that,

$$L = \frac{u_м}{u_c - u_м} l_c = l_c \sqrt{\frac{\rho_c}{\rho_м}}. \tag{9.49}$$

Thus, according to hydrodynamic theory, the depth of piercing is proportional to the length of the cumulative stream and to the square root of the ratio of densities of the stream and barrier. This depth does not depend explicitly on u_s; the greater the velocity of the stream, the faster it penetrates, but at the same time, the more rapidly it is exhausted.

The given formula, of course, is idealized, but it in general agrees with experiment. It is necessary only to consider that l_s cannot be set equal to the initial length of generatri of the cone l. If in the formula we substitute the magnitude l, then the actual depth of penetration will appear 2-4 times larger than by calculation. The fact is that, as already was noted, the cumulative stream is stretched with motion and $l_s > l$. Precisely for this reason, the greatest depth of piercing is obtained in that case, where the barrier is at a certain distance from the lowest section of the shaped charge; besides, the stream has sufficient time to be elongated. With further increases of distance, the stream loses stability, bursts, and expands, so that its piercing action drops sharply. Let us note that that distance from the charge to the barrier, at which stream has the biggest breakthrough capability is sometimes conditionally called the <u>focal length</u> of the shaped charge.

For a more precise definition of the theory of piercing, it is necessary to consider such factors strength, compressibility of the material of the stream and barrier, the force of internal friction, and viscosity. The diameter of the hole, formed during the spreading of the barrier material usually significantly exceeds the diameter of the stream and depends on the value of energy of the stream per unit depth of penetration and on the strength and fluidity of the barrier material. Holes in lead are significantly wider than in steel, although the depths of piercing for both metals are close.

The length of the cumulative stream, on which the depth of piercing essentially depends, theoretically should increase with increasing of height of recession, and also with increasing of diameter of the recession at its base. In practice, we usually employ conical recessions with a diameter, almost equal to the diameter of the lower part of the charge, and with a height, equal to 1-1 1/2 diameters (an angle $\alpha \approx 30\text{-}40^{\circ}$). Charges with a recession of large height give a stream of low stability. Conical recessions are effective and are convenient.

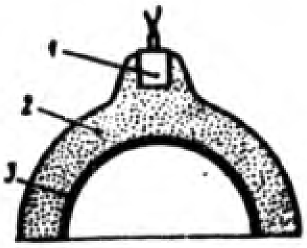

Fig. 9.20. Diagram of shaped charge with recession in the shape of a hemisphere. 1) detonator, 2) explosive charge, 3) metallic facing.

Sometimes one employs cumulative recessions (with facing) of other forms as well. Recessions in the form of a hemisphere (Fig. 9.20) are used in those cases, where maximum destructive action is to be obtained at a large distance from the lowest section of the charge; for hemispheric recessions, the focus of the cumulative stream is further removed from the lower section of the charge than in charges with a conical recession.

The properties of the cumulative stream and, in particular, its piercing ability, depend also on the facing material and its thickness. Both excessive and insufficient thicknesses of facings are undesirable. In practice one employs steel, copper, aluminum, and other facing materials; their thickness depends upon the dimensions and design of the charge, varying from 0.5 to 3 mm.

The properties of the cumulative stream and, in particular, its breakthrough action, depend also on the properties of the explosive.

For substances of low density and low rate of detonation the cumulative effect is weakly manifested. In order for cumulative effects to be most pronounced, it is necessary to use explosives of maximum density and rate of detonation.

With the aid of cumulation it is possible effectively to govern the phenomenon of explosion, and to obtain, at least in small volumes, concentrations of energy and pressures, greater than in products of explosion of the actual explosive, as well as to obtain a directed effect of explosion, in which action in given direction is significantly intensified over a limited area. All this makes the problem of cumulation very interesting from both the scientific, and the practical standpoint. With further elaboration of this important and promising trend in the physics of explosions, one can expect new and very valuable results.

CHAPTER X

THEORY OF SAFETY EXPLOSIVES

§ 1. Requirements for Coal Mine Explosives

A significant number of coal mines are explosive, or, as they are sometimes called, — dangerous with respect to gas and dust. In the extraction of coal, into the atomsphere of such mines are released combustible gases, the main component part of which is methane. With air, methane forms explosive, easily flammable mixtures. In the breaking, loading, and transportation of coal, coal dust will form. Suspended in air, this dust also can explode.

Explosions of dust frequently occur on a large scale. Methane is easily removed by ventilation, and dangerous concentrations of it can be created, as a rule, only at the stope. Therefore, the explosive gas usually has local character. Coal dust frequently covers the surface of excavations almost over their entire extent, and, once having started, a dust explosion can spread over the entire mine.

Among the causes, producing explosions of methane and dust in mines, blastings has always occupied a special place, mainly by virtue of the scale of accidents. An electrical spark, faulty lamps, etc., usually produce only local flashes of methane; but with the detonation of explosive charges in blast holes, large surfaces of the coal mass are bared, frequently with strong gas generation and significant fluctuations of pressure; this leads to the mixing of methane with air, and also to the rising of coal dust in the air, as a result of which, frequently large explosions often occur. Thus, in the 7 years (1881-1887) in France, there occurred 95 explosions of gas and dust in mines; of these, only 36 were often blasting; however, the number of victims in these 36 explosions in exceeded by 6 times the number of victims in all remaining explosions.

To prevent gas and dust explosions, mining operations are conducted in such a way as to prevent the possibility of methane accumulation in dangerous concentrations, and to reduce the explosiveness of coal dust, and, finally, to terminate an explosion before it has a chance to spread. This is done by ventilating underground excavations, selecting special excavation systems, which reduce or localize gas evolution and facilitate ventilation, maintaining constant surveillance over the mine atmosphere, limiting the use of electrical power and blasting under the most dangerous conditions, the removal of coal mines and dust, settling of coal dust with powdered slate, and irrigation, installation of slate gates, etc.

However, all these measures do not guarantee the prevention of formation of an explosive gas-air or dust-air mixture. Therefore, for blasting in coal mines is dangerous because of gas or dust it is permitted to use only the so-called special safety explosives.* The main distinctive peculiarity of these explosives is their lowered ability to produce explosion of methane-air and dust-air mixtures during blasting.

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*Earlier in our literature, such explosives were called anti-grisou explosives, from the French word grisou, meaning methane.

The expediency of developing safety explosives became clear, when it was established that such explosives as black powder or dynamite, which were widely used in their own time in coal mines, ignite comparatively easily the dust-air and, especially the methane-air mixture. An explosion of open charge of black powder of a weight of less than one gram, or several grams of dynamite, is sufficient to ignite the gas. Similarly with explosions in the open channel of a steel mortar, a 100-gram charge of shown explosives is sufficient to ignite the dust-air cloud.

In the explosion of an explosive charge in a blast hole, drilled in breed, one observes a number of phenomena, affecting the surrounding gas medium. The detonation, passing the explosive charge, evokes in the free part of blast hole* shock wave, which spreads with a velocity of several kilometers per second. After the shock wave gases, heated to high temperature and strongly compressed emerge from the blast hole expand. These gases mix with the surrounding gas medium and heat it. The shock wave, passing through the air, as a result of strong compression produces its glow; the gasiform products of explosion also glow due to their own high temperature, and also as a result of chemiluminescence. These glow phenomena make up to the so-called <u>flame of explosion</u>. Together with the gases from blast hole, hard particles of various types also emerge: particles of inert salts, entering into the composition of the explosive or formed during the reaction, and particles of the explosive itself, which have not reacted in completely the blast hole and continue to burn in flight.

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*Here we are considering the elementary case of an explosive in a blast hole without stemming, not accompanied by the destruction of the rock mass.

It is necessary to add, that gases, as a rule, consist not only in products of the full transformation explosives, but contain, depending upon the conditions of explosion, larger or smaller quantities of intermediate products.

All enumerated phenomena can in this or that degree promote the ignition of the methane-air mixture by the explosion. The multiplicity of factors, producing the explosion of gas, the complexity of calculation of their joint action, and the possibility of different mechanisms of ignition in various conditions of detonation, contribute to the difficulty of creation of a theory of safety explosives. Despite the fact that the study of this question has been conducted in various countries for almost one hundred years, such a theory still is far from completion. Various hypotheses ascribe the decisive role in the process of ignition to various factors from among those indicated above or to a combination of several of them. Before turning to a consideration of the mechanism of gas ignition in an explosion, let us describe some experimental methods of evaluating the safety of safety explosives.

§ 2. Methods of Testing Safety Explosives

In connection with the insufficient reliability of the theoretical appraisal of degree of safety explosives, experimental methods have long since begun to be used for this purpose. The most wide-spread method is the experimental drift test, The considerations on the basis of which were developed the first techniques of tests in an experimental drift, consist in the following.

The temperature of the products of explosion of explosives applied in technology is significantly higher than the minimum temperature of self-ignition of the methane-air mixture. Therefore, any explosive can in principle produce an explosion of firedamp. However, under real conditions of explosion, the gasiform products are cooled at the expense of work, as well as at the expense of heat radiation to the outside. The smaller the explosive charge, the relatively stronger will be this cooling, and as assumed, the less will be the danger of ignition of methane-air mixture in explosion of such charge. From this was drawn the conclusion that for every explosive, there should exist certain minimum quantity of charge, some limiting charge. The explosion of charges of less than limiting size must not ignite the methane-air mixture. As the comparative characteristic of properties of safety explosives was taken the size of the limiting charge, determined experimentally. The limiting charge is determined in an experimental drift, with explosion produced under conditions, as similar as possible to conditions of production blastings.

The designs of experimental drifts and the conditions of tests in them are different in various countries. Let us consider first the experimental drift of the Makeyevskiy Scientific Research Institute of Mining Industry Safety (MakNII), where all soviet safety explosives are tested.

The experimental drift of the MakNII (Fig. 10.1) consists of a cylindrical steel pipe 1.65 m, in diameter and 15 m, in length, closed off at one end by a strong bottom lid. The part of the pipe at the bottom with a volume of about 10 m^3, is called the detonated chamber; before the experiment it is partitioned off by means of a paper diaphragm. In explosive chamber is filled with methane to such a level, that the most dangerous methane-air mixture (8-10% CH_4 by volume) is formed. The explosive charge in cartridges 30-32 mm in diameter, is placed in the channel of the thick-walled steel mortar

(Fig. 10.2), which is mounted on a cart. Before the start of the experiment, the mortar is rolled close to a special crater in the bottom of the drift. After a methane-air mixture of the proper concentration is created in the drift, the charge is detonated.

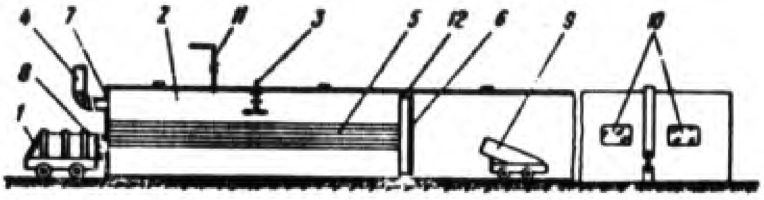

Fig. 10.1. Experimental drift of the MakNII for testing of safety explosives (diagram). 1) mortar; 2) detonating chamber of drift; 3) mixer; 4) ventilation pipe; 5) dust shelves; 6) paper diaphragm; 7) bottom lid of drift; 8) hatch in bottom lid of drift; 9) mortar for coal dust; 10) hatches for observation of flame; 11) gas intake; 12) rings for fastening paper diaphragm.

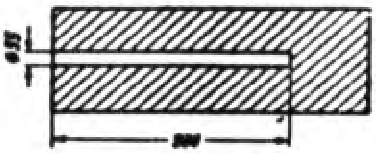

Fig. 10.2. Mortar for testing of safety explosives in experimental drift.

In order to determine the limiting charge, the tests were started from charge of 350 g which in the event of non-ignition, was consecutively increased in subsequent experiments to 100 g, not exceeding 650 g, since larger charges would strongly damage the mortar. The limiting charge was the maximum charge not producing ignition in 10 successive trials. Only those explosives, for which limiting charge was larger than 450 g were considered safety explosives.

In testing for dust safety, since dust, as a rule, ignites by explosion less readily than gas, it was strewn on shelves installed for this purpose in the drift, and also scattered in the drift.*

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*Since 1954, in order to assure the conversion of dust into the suspended state, it is ejected into the detonation chamber of the drift several seconds prior to the explosion of the test charge. This ejection is produced by the explosion of a small explosive charge in a special mortar, whose channel is directed toward the bottom of the drift (see Fig. 10.1).

In part of the experiments, a definite quantity of dust was placed in the channel of the mortar together with the explosive cartridge. The tests involve dust of a definite sort of coal and even coal from a definite layer, crushed to a definite degree of fineness. The total amount of dust is such, so that each m^3 of the explosive chamber of the drift contained 350 g of it. In such conditions, a determination was made of the maximum charge, not producing ignition of dust in several (usually 5) successive trials.

In recent years, we have introduced certain changes into the testing method (see GOST 7140-54). On the one hand, the test conditions have been made substantially less rigid (application of small clay stemming in experiments on gas, decrease in the number of parallel experiments in certain tests, etc). On the other hand, the limiting charge is no longer determined and that explosive is considered to be safe, which does not produce ignition of gas in the explosion with stemming of charges 600 g in weight and dust with a charge weight of 700 g.

In the development and introduction of the method of evaluating safety explosives for gas and dust in an experimental drift it was assumed that test conditions in it reproduce the most dangerous of conditions of blasting possible in practice. The charge explodes without stemming and the mortar channel is not destroyed, so that gases of explosion enter methane-air mixture, without accomplishing work, and in a hot state. From these considerations it was considered possible for blasting in mines to allow the use of charges of larger magnitude than the limiting charge, determined in the experimental drift.

Further research showed, however, that the influence of different factors on the possibility of methane ignition in an explosion more complicated than first supposed, and test conditions in the experimental drift are difficult to compare with conditions of blasting in mines and are by no means not always the most dangerous.

Thus, it was established that if in an experimental drift the danger of methane inflammation is increased with an increase in the charge, then in the experimental mine, where the conditions of explosion were closest to industrial, on the contrary, with large charges the danger of ignition is less. Further it was shown that the probability of ignition of the methane-air mixture depends on the length of the free space — distance from the mouth of the blast hole to the charge. Besides, for safety explosives of the ammonite class both small and large lengths of free space turn out to be safe; for nitroglycerine safety explosives, on the contrary, only small lengths of free space are dangerous. In the coordinate system "length of free space — size of charge" dangerous zones according to Beyling (Beiling?) are shown by the shaded sections in Figs. 10.3 and 10.4.

At last, according to the elementary considerations, indicated above, it was assumed that the application of stemming can only decrease the danger of methane ignition, since its ejection takes up part of the energy, and the temperature of gases of explosion is lowered. In reality, in certain cases the application of small stemming led to the inflagration of the methane-air mixture under conditions, under which it did not arise without stemming.

Among the deficiencies of the test in the experimental drift is also the fact that it essentially has a qualitative character. On the basis of these tests it is possible to say only that a given explosive satisfies or does not satisfy certain fixed requirements, but it is impossible quantitatively to estimate the degree of safety and compare different explosives on the basis of this criterion. With the aim of eliminating this deficiency, the US Bureau of Mines developed the method of characterizing safety explosives by the so-called "oxygen number."

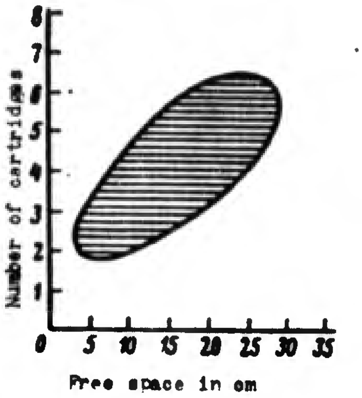

Fig. 10.3. Ignition region (shaded) for safety ammonite as a function of the number of cartridges (size of charge) and length of free space.

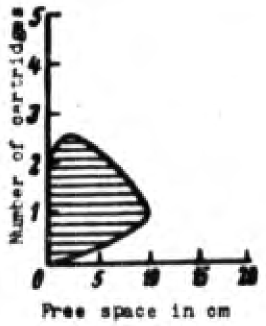

Fig. 10.4. Ignition region (shaded) for safety explosives on the basis gelatinized nitroglycerine as a function of the number of cartridges (size of charge) and length of free space.

It was established that with constant methane content (8%) in mixture of it with nitrogen and oxygen, the possibility of inflagration of the gas mixture in an explosion of a charge in an experimental drift influences the oxygen content. If it is higher than a certain limit, ignition is observed in all experiments; with an oxygen content lower than certain lower limit, ignition does not occur. Between the limits, it occurs with a certain probability, depending on content of oxygen in the atmosphere of the experimental drift. The more dangerous the explosive, the less oxygen should be contained in the mixture in order for the explosion of the explosive to produce its ignition.

Tests are performed on explosive charges weighing 3 g, which are pressed into small steel mortars 12.5 cm in length and 7.5 cm in diameter; the mortar channel has a diameter of 8 mm. The explosion is produced in a small drift (0.9 × 0.9 × 1.5 m). The characteristic of the explosive is the oxygen content in the methane-nitrogen-oxygen mixture, for which the frequency of ignitions of the gas constitutes 50%. If the explosive produces explosions with a frequency, equal to 1/2, with an oxygen content of less than 18%, it is considered very dangerous, while if 30.5 and more percent of oxygen are required, it is not dangerous. Black powder, dynamite No. 5 (50% nitroglycerine, 49% kieselguhr, and 1% chalk) and PETN, according to this test are the most dangerous explosives; the oxygen number for them is equal to 15.5.

The method of evaluation of safety explosives by the "oxygen number" has not yet been applied.

In the course of research in Germany, it was established that the danger of ignition of the methane-air mixture strongly increases in that case, where the explosive charge detonates not in the mortar channel, but in the open in the methane-air mixture. This danger becomes still greater, if near charge there is a barrier, at which there occurs the retardation of the expanded products of explosion. Inasmuch as such conditions can arise in mines, especially in blasting with electrodetonators delayed-action, it was expedient to realize them and in explosive tests. This was done in West Germany, and later in Belgium in the form of a test in a mortar-groove in the presence of a barrier. The mortar used was a steel cylinder 23 cm in diameter and 2 m in length with a cutout forming a groove, the shape of which is shown in Fig. 10.5. In this cutout was placed the test charge. The mortar was mounted at a definite distance from vertical steel wall; by turning the mortar on its support it is also possible to change angle α, formed by the plane of the groove with the wall. The limiting charge, determined under these conditions, is greater, the greater the distance d (see Fig. 10.5) and the smaller angle α.

On the basis of this method of test were determined requirements for explosives, allowed for use at present in West Germany. According to these requirements, safety explosives are divided into three classes. Explosives in the first class are more dangerous than those in the second, and those in the second — more dangerous than those in the third. The first class is comprised of explosives which sustain the gas test in an experimental drift with the detonation without stemming in the channel of a standard mortar of charges of length of up to 50 cm.* Furthermore, expansion in a Trauzl bomb should not exceed certain definite limits, depending on composition. In the mortar-groove explosives in the first class produce an explosion of gas already with a charge of one cartridge. This is also the behavior of safety explosives of the first class in standard inert safety shells. Explosives of the second class are tested in the mortar-groove. With a distance to the wall of 65 cm and an angle α = 40° they must not ignite gas with a

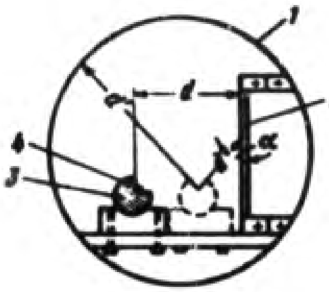

Fig. 10.5. Diagram of device for testing of safety explosives in an experimental drift with mortar-groove. 1) experimental drift, 2) reflecting wall, 3) mortar-groove, 4) explosive charge.

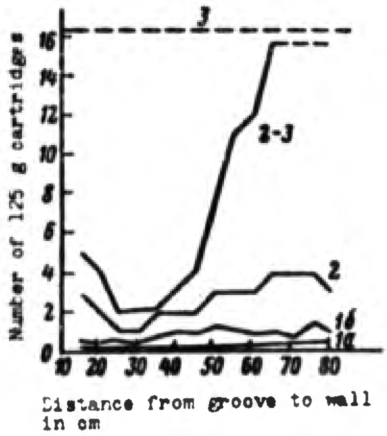

Fig. 10.6. Ability of various safety explosives to ignite methane-air mixtures in testing in mortar-groove (least number of cartridges, producing ignition with an angle α = 90° and various distances d from the edge of the groove to the wall). 1a) gelatinous explosives without safety shell; 1b) explosives with large content of salt, but without safety shell; 2) explosives with active safety shell; 2-3) (transitional type) explosives with increased active safety shell; 3) bicarbite or composition with 15% nitroglycerine on the basis of selective detonation (ignition lacking even with charge on 16 cartridges).

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*With a cartridge diameter of 35 mm this corresponds to a cartridge weight of 600 g.

charge of length 40 cm. Safety explosives of the third class must not ignite the gas with a charge of maximum length (2m), consisting of 16 cartridges (total weight 2 kg), with a carbon angle of $\alpha = 90^{\circ}$ and distances d from 15 to 75 cm.

Results of tests of various types of explosives are shown in Fig. 10.6. The characteristics of these mixtures will be given below (see p. 747).

The causes of the existence of the limiting charge with testing in a mortar-groove are not clear to the authors of this method. It is possible that with lengthening of the charge, there is an intensification of the effect of addition of shock waves, formed by explosion of consecutively placed cartridges. With a certain critical length of charge, the pressure at the barrier and the duration of its presence attain magnitudes, sufficient for the ignition of the methane-air mixture. They can act also indirectly as well, strengthening the heating of products of incomplete transformation, which scatter during the explosion and are braked at the wall.

§ 3. Mechanism of Ignition of the Methane-Air Mixture in Explosions

From the two basic hypotheses regarding the mechanism of ignition of the methane-air mixture, one (let us call it thermal) considers heating as the main factor in ignition; the other hypothesis ascribes a large role not only to thermal, but also to the chemical side of the development of ignition.

1. Thermal Hypothesis of Ignition Mechanism

The first research in the development of safety explosives was conducted in France Malliard and le Chatelier, which approached the solution of problem as follows they established experimentally that self-ignition of methane-air mixtures occurs with a significant delay. The minimum temperature, at which still self-ignition is still observed is equal to 650°C, and the delay with this temperature constitutes 10 sec. With increasing temperature, the delay decreases; at 1000°C it is equal to 1 sec, and with 2200°C becomes negligibly small.* Hence Malliard and le Chatelier concluded that unconditionally dangerous from the standpoint of ignition of firedamp will be those explosives whose temperature of explosion lies higher than 2200°C. At lower temperatures, the possibility of ignition of the methane-air mixture is determined by the time of action on it of the high temperature. If the time of action is greater than the delay of the flash at this temperature, then the explosion will ignite the gas. Hence, becomes understandable the high igniting ability of powder; not being able to detonate, it gives a flame of very great duration and therefore, easily ignites the gas.

In the explosion of explosives, especially under conditions of destruction of the rock, gases cool very fast. Therefore, as Malliard and le Chatelier supposed, in order to insure the practical safety of blasting for coal, sufficiently to lower the temperature of explosion to 1500°C; in operations involving rocks, where, as was assumed,

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*It is necessary to point out that according to the latest experiments of Audibert, the delay of self-ignition of the methane-air mixture is not an inevitable occurrence accompanying this phenomenon, but is rather caused by state of walls of vessel, in which the mixture is contained. If this conclusion is confirmed by further research, then it will be necessary to re-examine essentially our notions of the mechamism of ignition of methane-air mixture in the detonation of explosives.

the probability of formation of explosive methane-air mixtures is somewhat less, explosives even with a temperature of explosion up to 1900°C are permissible.

Subsequently, these ideas received elaboration, in the works of French researcher Audibert. He considered that the heating up of the methane-air mixture occurs by means of its mixing with gases of explosion. With mixing, the content of methane and oxygen in the forming triple mixture (methane-air products of explosion) drops, and its temperature increases. If in the process of mixing the following two conditions turn out to be satisfied: 1) the content of methane will be within the interval of combustibility; 2) the temperature will be higher than minimum flash point (this temperature is practically independent of the composition of the mixture and lies near 650°C), then flashing occurs. Audibert showed that the more oxygen there is in the products of explosion, the less it is necessary to add to them methane-air mixture, in order to obtain an explosive mixture. If the gases of explosion do not contain oxygen, then in order that ignition might occur by the indicated mechanism, their enthalpy q per mole of gases for explosives usual of the composition should be equal to 21.5 kilocalories. With the content in the gases of explosion of a fraction n of oxygen, the heat content required for detonation drops to

$$q=21,5-75n, \tag{10.1}$$

where q is in kilocalories/mole, and n is the molar fraction of oxygen per mole of gaseous products of explosion.

Thus, the criterion of safety explosives with a positive oxygen balance according to Audibert may be represented in the form

$$q<21,5-75n. \tag{10.1a}$$

Inasmuch as to obtain the greatest explosive effect it is desirable, that heat of explosion be maximum, it is expedient to recalculate the composition of safety explosives for zero oxygen balance $(n = 0)$.

In connection with the fact that heat of explosion of the usual explosives used in technology is significantly larger than the indicated limit, it is necessary for their transformation into safety explosives to artificially decrease it. This is effected by the dilution of explosives with inert materials not participating in explosion, of which the most frequently used are sodium and potassium chloride. On heating of impurities in an explosion is expended part of the heat, at the expense of which are lowered the enthalpy and temperature of gases.

As shown by experience, sodium-containing safety explosives, the calculated enthalpy of products of explosion of which is less than is accounted for by equation (10.1a), possess a high degree of safety. Therefore, the application of the given method for the calculation of the compositions of safety explosives is practically expedient. However, theoretically it is impossible to consider it fully founded. At the temperature of ignition, from which the calculation originates, the delay time attains 10 sec; during that time gases will continue to mix with the methane-air atmosphere and will have time to cool far below the minimum flash temperature. In general, if the detonation occurs by the mechanism of mixing and is characterized by a significant delay, then it should very strongly depend on the speed and conditions of mixing. Further experiments (A. I. Gol'binder) showed that it matters a great deal, which salt is introduced into the composition of the explosive. If we replace, for instance, sodium chloride alumopotash alum, ammonium chloride, and others, then danger of ignition of the methane-air mixture is strongly increased.

The overwhelming majority of explosives used in dangerous conditions with respect to gas and dust in the coal mines of different countries, do not satisfy the criterion of safety (10.1a) and theoretically are able to ignite the methane-air mixutre, although they withstand the experimental-drift test.* Certain explosives, which according to theoretical calculation, should not ignite gas, actually evoke its ignition under certain conditions, for instance, during the explosion of open charges.

2. Other Hypotheses About the Mechanism of Ignition of the Methane-Air Mixture in the Explosion of Explosives

In the explosion of a charge in a mortar or in a blast hole without stemming together with gases, there departs a certain quantity of undecomposed explosive particles. The German researcher Beyling defined in his connection with this the assumption to the effect that the decisive factor, determining the ignition of the methane-air mixture, is the entry to it of burning explosive particles. From this standpoint he explained the regularities, established in experimental research on the ignition of gas by the explosion (Fig. 10.3 and 10.4). The role of the size of the charge is determined according to Beyling by the fact that in the explosion of a large charge at the mouth of the blast hole there will form a cloud of gases of large

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*Audibert explains this by the fact that in explosions in a mortar without stemming, chemical reactions do not go to the end, and therefore, heat and temperature of explosion are obtained lower. Furtnermore, especially with small charges, i.e., with a large free space, part of heat is conveyed by the gases to the metal and they emerge from the channel of the mortar already somewhat cooled.

dimensions, flying through which, the burning explosive particles burn up before they enter the methane-air atmosphere.

The peculiar influence of free space in the case of ammonite Beyling explains by the fact that these explosives in contrast to nitroglycerine give initially incombustible particles therefore not capable of igniting methane. Only after flying a certain distance in the blast hole in an atmosphere of hot gases of explosion, the particle ignite and then become dangerous. The effect of a small stemming in favoring ignition is explained in a similar way.

The considerations put forth by Beyling regarding the possibility of entry into the methane-air mixture during blasting of decomposed explosive particles will agree with the contemporary notion about the mechanism of explosion of hard, especially of powdery substances. Apparently, also valid is his assumption about the great effectiveness of burning explosive particles, which scatter in an explosion, in the sense of the possibility of ignition by them of the methane-air mixture. However, the role of these particles Beyling conceives too simply.

At first glance, the ability of burning explosive particles, flying with great speed, to ignite the methane-air mixture more easily than do gasiform products detonation is incomprehensible. It is obvious that the temperature of the products of burning cannot be higher than the temperature of detonation. In the first place, in the detonational wave there is developed a large pressure and reactions go to completion, which cannot occur with the burning of particles under lower pressures. Accordingly, in accordance with the thermal effect of detonation is usually larger than that of burning at moderate pressures. Secondly, detonation is an extraordinarily brief process and it is possible to suppose that gases during its occurence do not succeed to convey heat to inert components of explosives. With the relatively slow burning of particles, the conditions for the cooling of gases are much more favorable and its role is relatively greater. Further, with detonation, the temperature of the gases, equal to $\sim Q_{det}/c_v$, is considerably higher than in combustion, when it is equal to $\sim Q_{bur}/c_p$, since $c_p > c_v$ and $Q_{det} > Q_{bur}$. At last, in case of fast-traveling particles, the duration of action of high temperature is so small that it is difficult to admit the possibility of ignition by them of the methane-air mixture, which proceeds with a significant log.

What in reality is the possible role of flying explosive particles in the ignition of methane?

In order to answer on this question, let us consider in more detail the process of explosion of safety explosives and those phenomena, which can affect the ignition of the methane-air mixture.

As was shown in Chapter IV, chemical transformation in detonation occurs in a certain layer of explosive final thickness. The reacting layer includes the final gasiform products of reactions, being under large pressure, and explosive particles, burning in atmosphere of compressed and heated gases. Burning proceeds with the formation of intermediate products. Due to the great pressure, present in the reacting layer, gases tend to be expanded. If conditions (absence of a thick shell, small diameter of charge, etc.) favor expansion, then a drop in pressure in the reacting layer can become so significant that chemical reactions, especially in the peripheral parts of charge, cannot reach completion, and the products of explosion will contain a large amount of intermediate gasiform products and even particles of unreacting explosives. Even gasiform and hard products can enter the methane-air mixture.

In order to more correctly estimate the possible role of burning explosive particles, let us consider certain data on the role of thermal and chemical factors in the process of methane ignition.

From theoretical considerations and from practice in the development of compositions of safety explosives it follows that the temperature of products of explosion is an essential, but not the only factor, determining the possibility of ignition of the methane-air mixture by explosions.

This conclusion maybe illustrated by the following experiments by Taffanel and Dautriche. They detonated in vessel of large volume (in a boiler) charges of trotyl and nitrocellulose. Both of these substances had a negative oxygen balance, forming in explosions significant quantities of combustible gases, mainly CO and H_2. Upon mixing with air, the products of explosion can ignite. The flash was observed under given conditions of the experiment according to the additional increase of pressure in the vessel at the expense of heat, separated during the combustion of CO and H_2. By this increase of pressure they calculated the total thermal effect of the explosion and final burning of its products in air. The results of the experiments are given in Table 10.1.

From Table 10.1 it is clear that if one were to detonate trotyl or nitrocellulose in pure form, then the combustion reactions go to completion. If to the explosive is added a small quantity (1-3%) of salts of alkali metals, then the combustion reactions are absent. With the addition in place of the above salts of alkali earth metal carbonates or lead nitrate, combustion occurs just as without additives. Undoubtedly, first of all, the cooling action of additives due to their low content is small; secondly, such oxygen-rich additives, as KNO_3, can increase the temperature of gases of explosion of trotyl and nitrocellulose at a higher rate, without lowering it. Thirdly, it is also clear that the addition of 10% $MgCO_3$ lowers the temperature, in any case more strongly than the addition of 1% $NaHCO_3$. At the same time, the second of these additives suppresses burning, while the first does not.

The experiments of Taffanel and Dautriche on the ignition of mixtures of carbon dioxide and hydrogen with air clearly indicate that along with heat absorption, certain "inert" additives play an active role, retarding the progression of reactions between combustible gases and atmospheric oxygen.

There are data on the effect of various inert salts on the ignition of direct mixtures of methane with air. In Table 10.2 are given results of experiments on the determination of the minimum quantity of various salts, which it is necessary to mix with the methane-air mixture, in order to prevent its ignition under certain conditions. From the table one may see that these quantities are highly distinct, and the most effective braking of the ignition of methane is provided by the salts of alkali metals.

The above experiments of A. I. Gol'binder, and subsequently the experiments of L. V. Dubnov showed that safety explosives with identical basic components and identical claculated temperatures of explosion turn out to be safe, when as the "inert" additive they contain halide salts of alkali metals, but ignite methane with the addition of quantities of other salts of equivalent heat capacity.

Table 10.1. The Effect of Additives to Nitrocellulose and to Trotyl of Different Salts on Final Combustion of Explosive Products in Air (According to Experiments of Taffanel and Dautriche)

Explosive	Addition	Separating quantity of heat per 100 g of explosive, kilocalories	Calculated quantity of heat per 100 g of explosive kilocalories
Nitrocellulose $C_{24}H_{30}O_{40}N_{10}$	Without addition	184	In detonation at about 96 kilocalories with detonation and full burning of its products at the expense of atmospheric oxygen, about 242 kilocalories
	0,5% $NaHCO_3$	146	
	1% $NaHCO_3$	88	
	2% $NaHCO_3$	89	
	2% KNO_3	88	
	3% K_2SO_4	79	
	2% $CaCO_3$	152	
	4% $MgCO_3$	152	
	10% $MgCO_3$	140	
	3% $Pb(NO_3)_2$	140	
Trotyl	Without addition	250	With detonation at about 66 kilocalories; with detonation and full burning of its products at the expense of atmospheric oxygen, 354 kilocalories
	2% KNO_3	117	
	3% KNO_3	96	
	4% KNO_3	82	
	5% KNO_3	66	
	10% KNO_3	66	
	6% $Ba(NO_3)_2$	187	
	10% $Ba(NO_3)_2$	175	

Table 10.2. Minimum Quantities (in milligram) of Various Salts Which Prevented Ignition of the Methane-Air Mixture

Substance	LiF	—	—	—
Quantity in milligrams	<1	—	—	—
Substance	NaF	NaCl	NaBr	NaJ
Quantity in milligrams	<1,5	<2	4—6	5—7
Substance	KF	KCl	KBr	KJ
Quantity in milligrams	1—2	8—9	8—9	9—10
Substance	CaF_2	Fluorspar	BaO	$BaCl_2$
Quantity in milligrams	2—3	<1	23—25	35—38
Substance	$Ba(NO_3)_2$	$BaSO_4$	Li_2SO_4	—
Quantity in milligrams	35—38	38—40	40—42	—

The effect of dust of alkali halides on ignition of methane-air and other explosive gas mixtures is fully explicable. The reactions of methane oxidation leading to self-ignition, are chain reactions, and the course of chain reactions is strongly influenced, as is known, by the hard surface, especially surface of such substances as halides of alkali metals. On such a surface many chain reactions are terminated quite efficiently, i.e., with high probability; the active centers of these reactions are deactivated and recombined.*

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*It is natural, therefore, that the minimum quantity of additive, necessary for preventing ignition, turns out to be all the less smaller than its particles. However, for various substances, the reduction of particle size for uncertain reasons has a quantitatively non-uniform effect: relatively weak for potassium salts – significantly stronger for sodium salts; for Al_2O_3 and SiO_2 it is almost undetectable.

In connection with the fact that the introduction into the composition of explosives of alkali metal halide salts lowers the danger of ignition of the methane-air mixture in an explosion much more strongly than many other inert salts, one should consider that ignition occurs by a chain mechanism in this case as well.

Inasmuch as the development of chain reactions of oxidation prior to ignition is strongly affected by active intermediate products, formed in the course of these reactions, it is natural to assume that a similar effect can be rendered by active products (or substances which easily produce them) upon their introduction from without as well. This is confirmed also by direct experiments. It has been established, that the ignition of a mixture of methane with air during heating is strongly affected by the addition of a number of substances. Thus, the addition of 2% formic acid or diazomethane lowers the temperature of self-ignition from 580 to 200° ; a similar effect is produced by various organic and mineral peroxides (ethylhydrogen peroxide, nitrogen dioxide, ClO_2) and certain other substances (methyl alcohol, ammonia, ethylene, etc.). Certain impurities (for instance, dimethylacetone with subsequent irradiation, producing its disintegration) lead to the self-ignition of the mixture of methane and air even at room temperature.

On the basis of these data, it is possible to assume that the basic role of burning explosive particles consists in the fact that they are a source of intermediate products of combustion directly introduced by particles during their flight in the methane-air mixture; this accelerates reactions leading to its ignition.

The assumption about such a role by decomposed explosive particles also has direct experimental confirmation. Very convincing in this respect is one of the experiments of Audibert. He let a small crystal of ammonium nitrate fall through a methane-air mixture heated to 375°C. Mixture was ignited, although, as is known, the minimum temperature of its self-ignition is equal to 650°C. The main purpose of the preliminary preheating of the mixture to 375°C was consisted in the fact of producing the decomposition of ammonium nitrate. The presence of products of this decomposition lowered the temperature of self-ignition of methane by almost 300°.

To check the possibility of ignition from burning particles of other explosives direct experiments were performed, in which small samples of different explosives were ignited in the atmosphere of methane-air mixture. If one were to assume that burning explosive particles during fast flight through the methane-air mixture can ignite it, then this is all the more true for motionless burning particles. Experiments showed that particles of various explosives strongly differ in their ability to ignite the methane-air mixture. Thus, detonating the lead azide in ignition does not ignite the gas even with significant charges (in pressed form — up to 600 mg); in contrast, mercury fulminate, which only burns in small quantities, produces ignition already in amounts of 0.2-0.4 mg, black powder (0.4-1.0 mg) also easily ignites methane. Particles of substances, which enter into the composition of safety explosives (trotyl, nitrocellulose, nitroglycerine), in usual conditions of combustion do not ignite the methane-air mixture even with substantial amounts (up to 1 g). If, however, there occurs not the burning, but the flashing of the explosive, then the ignition is observed already from a sample of, in the case of gelatinized nitroglycerine, for example, of 1 mg, while in the case of burning, it is not produced even with the largest test sample of this explosive — 130 mg. The most probable reason for this is the possibility of entry during the flash of active intermediate products directly into the methane-air mixture; during usual burning, conditions for mixing of these products with the medium are less favorable.

Thus, experimental data in accordance with theoretical considerations show that decomposed or burning explosive particles under certain conditions of burning can be a cause of ignition of the methane-air mixture.*

Especially favorable conditions for the entry of decomposed explosive particles into the surrounding methane-air mixture are created in the explosion of (completely or partially) open charges, when scattering of particles, especially from the periphery charge, is great. Therefore, although under these conditions transformation is incomplete and the heat and temperature of the products of explosion are relatively low, the danger of ignition of the methane-air mixture turns out to be significantly larger than during the detonation of an explosive charge in a mortar.

Let us add that on the basis of the hypothesis of the role of combustible particles, it is possible to give a natural explanation of many of the particular dependences of ignition of methane, found by Beyling (effect of stemming, /location of initiator,/ magnitude of charge, magnitude of

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*Similar experiments, carried out on a hydrogen-oxygen mixture, showed that it is easily ignited by lead azide as well as mercury fulminate and lead trinitroresorcinate. Relatively easily ignition of this mixture is also produced by secondary explosives (fulminate jelly, nitrocellulose). Distinction of the hydrogen mixture from the methane mixture is determined, apparently, not only by the lower temperature of its ignition but in the first place by the significantly less pronounced delay of flash.

free space, etc.). All of the factors, promoting the completion of reactions of explosion up to the emergence of its products from the blast hole, decrease danger of ignition. This includes first of all the application of stemming, which retards the expansion of gases of explosion and thus promoting the completion of reactions. As shown by experience, in many cases it is sufficient to have even small stemming, the expenditure of energy on its ejection being relatively small. For this reason, the danger of a blank explosion cannot be explained only by the fact that during it, gases of explosion enter the methane-air atmosphere without accomplishment of work. A very important role is played, undoubtedly, by the content of active intermediate products.

What sort of role in the light of the above notions might one ascribe to "inert" additives?

This role is threefold. First of all, the particles of "inert" additives on being heated at the expense of the heat of explosion, lower its temperature; secondly, in the mixing of products of explosion with the methane-air mixture, additives retard and disrupt the chains, and the development of reactions of methane oxidation leading to the ignition of the mixture. Thirdly, as is shown by the latest studies, "inert" additives affect some of the reactions occurring during explosions, promoting their full progression, and thus, lower the content in the products of explosion of active intermediate products, which supposedly promote the ignition of the methane-air mixture.

The conclusion regarding this third function of "inert" additives is based on experiments, which showed that such materials as sodium chloride or potassium chloride, are positive catalysts of combustion of certain explosives, sharply increasing the speed and combustability of ammonium nitrate and its mixtures. Under the influence of such additions there is also a change in the composition of the forming gases: their content of products of incomplete combustion, in particular, oxides of nitrogen, decreases. A similar effect of additives on the composition of products of reaction is observed and in explosions.

From these data and considerations there follows the additional criterion of suitability of a given substance as an "inert" additive: such substance should be not only a heat absorber (this ability is possessed, in general, by any substance) and a negative catalyst for reactions of methane ignition, but also a positive catalyst for reactions of combustion of the given explosive.

Employed additives such as NaCl and KCl turn out to be effective in all three ways. It is possible that there exist additives which still strongly accelerate the combustion of explosives and in still greater degree lowering, in combination with other additives, the danger of ignition of methane-air mixtures.

It is necessary, however, to bear in mind that the effect of additives, stimulating the complete burning of explosives under certain conditions can affect the safety of blasting negatively as well.

Let us imagine a practically possible case, when in the detonation wave, chemical transformation has affected only the most reactive portion of the explosive components, as is the case in compositions, prepared according to the principle of selective detonation (see p. 742). The temperature attainable here is so low that the products of explosion cannot ignite the methane-air mixture, even if they enter without accomplishing work. If an explosive contains additives, promoting "burning to completion," chemical transformation becomes more complete, the temperature can increase strongly and there will be created a danger of methane ignition.

§ 4. Ignition of Dust-Air Mixtures in Explosions

The ignition of dust-air mixture in explosions has been studied much less than the ignition of the methane-air mixture. An essential role in the case of dust ignition is played by the shock wave and the flow of expanded gases of explosion, promoting the rising of dust and formation of the dust-air cloud. Furthermore, producing compression (and consequently, the heating) of the dust-air suspension, they facilitate its ignition.

The basic source of coal dust ignition are assumed to be hot gases of explosion, especially if reactions in them did not succeed in going to completion. A characteristic of the danger of such gases is the magnitude and duration of the flame of explosion.

The flame of explosion* heats the dust-air suspension, producing the separation from the dust of combustible gases; the mixture of these gases with air produces a flash which then spreads from layer to layer.

Very dangerous with respect to dust ignition are safety explosives with a strongly negative oxygen balance, used at one time in Germany.

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*Let us add that previously, the flame of explosion was assigned great importance also with respect to the ignition of methane. Subsequently it was established that magnitude of flame changes strongly on the conditions of explosion, where frequently those conditions, which give a large flame, turn out to be less dangerous with respect to gas ignition. Moreover, the actual nature of glow during detonation may be different. Therefore, at the present time, the flame of explosion as a criterion of the danger of methane ignition has lost its previous significance. The problem of the nature of light phenomena in explosions and their relation to the safety properties of explosives will be considered below in greater detail (see § 7, heading 1).

Such explosives, forming much carbon monoxide and hydrogen, giving a large and prolonged secondary flame, and easily igniting the dust-air mixture.

Especially dangerous with respect to ignition are the practically possible cases, when coal dust is in the blast hole and in direct contact with charge. In such conditions, dust easily interacts with the hot products of explosion. As a result, there are formed significant quantities of combustible gases, which leads to appearance of the secondary flame, that ignites the dust-air mixture. As shown by experiments in the experimental drift, highly dangerous under conditions of contact of dust with cartridges are those explosives, which contain significant quantities of relatively slowly decomposed potassium or sodium nitrate.

Modern safety explosives, almost always having an oxygen balance, close to zero, if they satisfy the safety requirements with respect to the ignition of gas, turn out to be, as a rule, safe with respect to dust as well.

§ 5. Principles of Composition of Safety Explosives

The above considerations lead to certain general principles of composition of safety explosives, which (consciously or empirically) have been reflected in practice.

The first requirement for such compositions consists in the limitation of the energy (heat) of explosion.

With a high energy of explosion, the gaseous products will have a higher temperature, which may be sufficient for the ignition of methane. Furthermore, with high energy, the explosive usually has a high speed of detonation and correspondingly produces a powerful shock wave in the surrounding atmosphere, temperature in the front of which can be much higher than the temperature of the gases of explosion. In this case, the ignition of methane may be produced as a result of the compression and heating by the shock wave.

In order to decrease energy of explosion, inert additives are introduced into the explosive. However, to lower the danger of ignition of the methane-air mixture solely at the expense of limitation of energy of explosion is practically unprofitable, since this energy determines also the efficiency of the explosive. For this reason for lowering of the temperature one employs not just any heat absorbers, but such which simultaneously catalytically increase the completeness of explosion and hinder the ingition of the methane-air mixture. Both of these factors sharply lower the danger of ignition of methane by gases at a given temperature as compared to the case, when the explosion and contact with methane occur in the absence of "inert" additives of a given type.

It is necessary to add that with a sufficiently low energy of explosion, it is expedient to attempt to obtain the highest possible speed of detonation, since thereby is attained the most complete transformation of the explosive into the final products and to a small concentration of intermediate active products in the gases of explosion. Simultaneously, this brings about an increase in the brisance of explosion, which is frequently desirable in work involving rocks of more than average toughness.

Finally, it is possible to decrease danger of ignition of a gas at the expense of incompleteness of transformation of the explosive in an explosion, by using components of lowered reactivity, coarse crushing, high explosive density, etc. If thereby the temperature of the gasiform products of explosion will be strongly lowered, then, in spite of the formation of active intermediate products of transformation, the ignition of methane-air mixture may not occur.

This way is inexpedient in the majority of cases, inasmuch as it involves with a lowering of the efficiency and, furthermore, is unreliable, since among the various conditions of blasting operations there can occur such, in which transformation in the explosion will be complete, whereupon there will occur the ignition of methane. Only in certain conditions of blasting, when it is difficult to insure safety by other means, does the lowering of danger of ignition at the expense of incompleteness of transformation of the explosive turn out to be an effective means and find application.

The probability of ignition of the gas is especially great in cases, when the explosive charge is partially or completely exposed and directly in contact with the methane-air mixture. Such cases can occur either when blast holes intersect cracks or slots in the coal bed, or when the number of charges are detonated in sequence and the action of some charges may lead to the exposure of others. Safety explosives of the usual type can be made safe under these conditions, if one were to introduce very much "inert" salt into them. Here, however, the efficiency of the explosive becomes extremely low.

The solution to the problem consists in the creation of so-called selectively detonating explosives, including components of sharply different reactivity. In such explosives, the primary transformation of the most reactive components occurs under any conditions of detonation (charge is open or enclosed in a blast hole). The components of lower reactivity will, however, enter into interaction only in the case where the transformation proceeds in a closed volume, and the pressure, created by the primary process, does not drop too fast. In this case, the gasiform products of the primary process have time to transmit the surplus of their internal heat to the less reactive components and to produce their interaction. The faster the primary reaction and the smaller the amount of liberated energy, the sharper the selectivity of detonation and the later the reaction of the low-reactivity components (if it occurs at all).

Thus, the total heat of reaction of selectively detonating explosives is liberated only when there is resistance to the expansion of gases, which the explosion should surmount. The surmounting of the resistance takes up part of energy; the temperature of the gases drops and there is a corresponding decrease of the possibility of ignition by them of the methane-air mixture. If, however, the charge is partially or completely bared and the gases can enter working atmosphere without performance of work, then even in this case they do not present a danger, since the temperature, attainable in the transformation of only the most reactive components, is too low for that while the remaining part of the explosive, as a result of the fast drop of pressure, will not react, playing the role of an inert heat-absorbing component.

In order to assure real safety, the selectivity of detonation should be high. With limited selectivity, the ignition of the methane-air mixture under the following conditions is possible.

Let us suppose that the gasiform products of an explosion, in expanding, move along a crack, present in the coal bed, and drag with them the unreacting low-reactivity explosive components. After passing a certain distance along the crack, the gases meet with some barrier, braking their motion. Due to braking, the kinetic energy of the gases goes into heat, the temperature and pressure increase and, if the reactivity of scattering part of the explosive is insufficiently small, its residue can react and ignite the methane-air mixture. Such behavior is especially typical for ammonium nitrate. The test in mortar-groove in the presence of a reflecting wall was introduced in order to take into account the danger of ignition during the above phenomenon.

Thus, basic principles of composition of safety explosives consist in the following:

a) limitation of temperature and heat of explosion, assured by the introduction of nonreactive salts;

b) use of nonreactive salts, which are negative catalysts of methane oxidation;

c) use of such a ratio of components, as corresponds to a zero oxygen to balance, excluding with complete transformation the formation of combustible gases and free oxygen;

d) use of principle of selective detonation to decrease the danger from the explosion of exposed charges.

Inasmuch as it is desirable to limit the heat (temperature) explosion, as the basic component of safety explosives ammonium nitrate is widely used. Mixtures using this base have a low heat of explosion,* so that initially in France, but then in Russia safety explosives were used, consisting simply of ammonium nitrate, sensitized through the addition of fuel or a more sensitive explosive.

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*The heat of explosion of ammonium nitrate constitutes just 378 kcal/kg; the heat of explosion of its mixture with carbon in the ratio of 93:7 (zero oxygen balance) is also low (893 kcal/kg).

Such were the stratium grisoutine (88% ammonium nitrate, 12% weakly-gelatinized nitroglycerine) and rock grisoutine (70-71% ammonium nitrate, 30-29% gelatinized nitroglycerine) and the Favier compositions (80-95% ammonium nitrate and 5-20% aromatic nitro compound — dinitronapthalene, dinitrobenzene, trinitronapthalene).

However, the use of all these mixtures not containing "inert" additives, is impractical, since the danger of ignition of the gas in their explosion decreases only at the expense of lowering the energy of explosion and remains sufficiently significant; furthermore, they have their own specific disadvantages. Thus, grisoutines have a strongly positive oxygen balance; this leads to the fact that the energy, which can be obtained at the expense of oxygen, liberated in the disintegration of the ammonium nitrate, is used incompletely; along with this, the content of oxygen in the gases of explosion, as was shown, increases the danger of ignition. The Favier compositions with zero oxygen balance have too high a temperature of explosion and, furthermore, are characterized by low susceptibility to detonation and significant caking.

To reduce their inherent deficiencies, contemporary safety explosives based on ammonium nitrate are prepared in such a manner that they have a zero oxygen balance and contain the most effective and accessible "inert" additives known today. Along with this they have to possess a sufficiently high detonational ability, in order to reduce to a minimum the quantity of explosive particles and products of its incomplete disintegration, entering the methane-air mixture. The heightened detonational sensitivity is attained by fine crushing of ammonium nitrate and fuel components and their thorough mixing with each other.

An effective means of increasing the detonational sensitivity of ammonites is the introduction into their composition of small quantities of highly sensitive explosive components (liquid or hard), nitroglycerine, nitroglycol, PETN, and so forth. Along with basic components, the composition of ammonites includes caking preventives (wood meal, stearates, etc), and lowering moisture-holding ability.

To increase the detonational ability of ammonites it is possible also to employ "inert" additives in the form of particles of large size. In such a form they hamper the passage of detonational waves in smaller degree; at the same time, fragmenting in the explosion, the additive executes its own positive functions; assures complete burning of the explosive and hampers the ignition of the methane-air mixture. Of course, here there is a known contradiction, the detonational sensitivity is higher, when the "inert" salt is introduced in the form of large crystals. The effectiveness of the salt in the sense of preventing methane flashing is even greater the finer it is crushed. Nonetheless, the reasonable use of this method, for instance the use of an "inert" additive in the form of lumps, consisting of small particles, permits an essential increase in the detonational ability of compositions with a large content of "inert" additives without damage to safety properties.

As an example of the composition of modern ammonites it is possible to cite ammonites III/1, PZhV-20, and III/2. Ammonite III/1 contains 56% ammonium nitrate, 9% trotyl, 3% wood meal, and 32% sodium chloride. Ammonite PZhV-20 contains 64% ammonium nitrate, 16% trotyl, and 20% sodium chloride. Ammonite III/2 contains 70% ammonium nitrate, 6% nitroglycerine, 2% dinitrotoluene, 3% wood meal, and 19% sodium chloride.*

Also known and still used in foreign countries are safety explosives, not containing ammonium nitrate. Their basic explosive component is gelatinized nitroglycerine; as the "inert" additive they contain the same sodium, as well as certain other salts of alkali metals. An advantage of such explosives as compared to ammonite is their high detonational ability and high brisance. Their essential deficiencies consist in heightened danger in handling and high cost. As an example of such substances it is possible to cite the English composition, containing 57-58% nitroglycerine, 3-3.5% collodion cotton, 5% sodium nitrate, 11% sodium chloride, and 21-22% borax.

Also used are mixed explosives, containing significant quantities of both ammonium nitrate and nitroglycerine. As an example it is possible to cite the German "Nobelite B," containing 30% gelatinized nitroglycerine, 26.5% ammonium nitrate, 0.5% wood meal, 3% aqueous 50% solution of calcium nitrate (to augment plasticity of the explosive), and 40% sodium chloride.

According to German researchers, the minimum danger of ignition of methane characterizes explosives prepared according to the principle of selective detonation. Such explosives contain a limited amount (up to 15%) of high-reactivity components, such as nitroglycerine, and a mixture of relatively coarse-grained powdery, slowly-reacting, nonexplosive components, one of which is the carrier of oxygen (e.g., $NaNO_3$) and the other — a fuel (e.g., wood meal). The interaction

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*Explosives of this type later came to be called "pobedites."

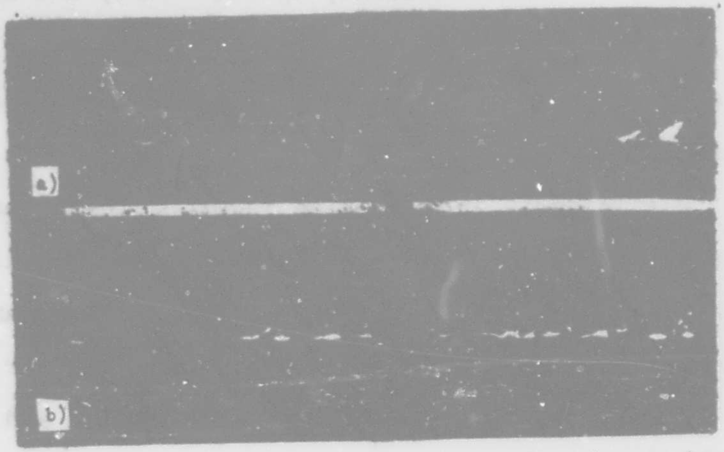

Fig. 10.7. Photograph of explosion in mortar-groove of explosives containing: a) 15% nitroglycerine and a mixture of sodium nitrate and wood meal; b) 15% nitroglycerine and inert salts only.

of the last two components occurs only at sufficiently high pressure. When a charge without durable shell explodes, the sodium nitrate and wood meal behave like inert components. Graphic proof of this is provided by a comparison of photographs (see Fig. 10.7) of an explosion in a mortar-groove of identical charges with 15% nitroglycerine, containing a mixture of sodium nitrate and meal (a) and inert salts only (b). The full similarity of the character of glow convincingly indicates that under the given conditions of explosion, sodium nitrate and wood meal act as "inert" additives. Still more graphically this is confirmed in experiments, in which were gathered the solid residues after explosion in the mortar-groove. These residues in significant measure consisted of unreacted wood meal and sodium nitrate, surviving the passage of detonational wave. The fact that in the presence of a durable shell they nevertheless react, shows the significant explosive action of explosives in these conditions. Of course, this action cannot be determined by the usual methods, in the Trauzl bomb, expansion constitutes for certain practically effective explosives just 100 cm^3; the cause of this consists in the insufficiency of resistance exerted by the sand stemming, in order for the interaction of the saltpeter and meal to proceed to completion. The interaction of components of low reactivity occurs only in a tough shell and with noticeable delay. In the case of low-percentage (with respect to nitroglycerine) mixtures, the speed of detonation in the transition from an explosion of a charge without a shell to an explosion in thin-walled (3 mm) iron tube increases only very insignificantly. It is necessary to have a thick-walled tube, so that the reaction between the saltpeter and meal might go to completion.

In another variant of an explosive of this type the fuel is partially replaced by ammonium chloride. This gives the advantage that sodium is formed in the course of transformation in an extremely fine state through the reaction

$$NH_4Cl + NaNO_3 \rightarrow NaCl + N_2 + 2H_2O + \frac{1}{2}O_2,$$

i.e., simultaneously with exothermal reactions of decomposition of ammonium nitrate and the interaction of the liberated oxygen with the fuel. These conditions are the most favorable for retarding sodium chloride of ignition of the methane-air mixture.

§ 6. Safety Shells and Explosive Substitutes in Blasting

In the above considered examples, the "inert" additive, lowering danger of ignition of the methane-air mixture, was introduced into the composition of the explosive. This method of application of the additive has that basic deficiency that due to the heating of the inert salt starting at an early stage of explosion, there is a drop in temperature and pressure of the gasiform products, but this hampers the propagation of the explosion. It is expedient therefore to create conditions in which the additive would interact with certain lag, after chemical reactions in the explosive have had time to be completed.

One of the paths, leading to this goal, is the application of "inert" additives in the form of so-called safety shells. The actual explosive can contain inert additives in moderate quantities or even none at all. A cartridge of such an explosive is placed in a shell several millimeters thick containing considerable amounts of an "inert" additive, usually the same alkaline chloride. In the explosion, the shell will be atomized and the resulting dust promotes the completion of reactions of transformation of the explosive, and then retards ignition of methane.

There are two types of safety shells, inert shells, not containing explosive components, and active safety shells, which, besides the "inert" base, contain small quantities of highly sensitive liquid explosive and represent a weak but very detonation-sensitive explosive. In the explosion of an explosive cartridge, placed in active safety shell, the latter also explodes. This promotes fuller and finer atomization of the "inert" salt, insuring its maximum effectiveness.

As material of the active shell, compositions of the bicarbite type — mistures containing as the explosive component nitroglycerine, and as the basic "inert" additive — sodium bicarbonate. Such a combination of components ensures very high detonational ability: a mixture, containing just 10% nitroglycerine, reliably explodes from a detonator-capsule. Bicarbonate is especially useful as an additive, lowering the temperature of the products of explosion, since it absorbs heat not only physically, being heated, but also as a result of endothermic decomposition. Usually into the composition of bicarbites there enters also a significant quantity of sodium chloride.

Being too weak for application as an independent explosive (expansion in lead bomb constitutes just several tens of cubic centimeters), the bicarbites as safety shells sharply lower the danger of ignition of the methane-air mixture. Such shells are essentially superior in this respect to inert safety shells also because the latter surround the explosive cartridges only over the lateral surfaces, while active shells also cover the butt ends. Therefore, with active shells the gasiform products of explosion cannot directly enter the surrounding atmosphere; with inert shells, on the other hand, this is not excluded on the butt ends of the charge.

The indicated distinctions are graphically shown in photographs of explosions of freely suspended charges in shells both types (Fig. 10.8). With the inert shell, on both ends of the charge are observed bursts of flame; with the charge in the active shell, the glow is weaker and its contours are limited to the charge contours.

The most wide-spread of explosive <u>substitutes</u> is cardox. It consists essentially of a durable steel tube, on one end of which is screwed a discharge, and on the other, an ignition head (Fig. 10.9). The discharge head is covered by a steel disk which is cut when a certain pressure (1300-2800 atm (tech.)) is attained in the tube. The ignition head has a valve for filling the tube with liquid carbonic acid and inputs for current, with the help of which the nonexplosive heating composition enclosed in a paper shell is ignited. The prepared cardox is introduced into the blast hole, drilled in the coal or rock. The heating composition is ignited by passage of current; the heating of the liquid carbon dioxide increases its pressure, the disk is cut away and the gases rushing through the discharge head crack the surrounding medium. Tube can withstand a large number of detonations.

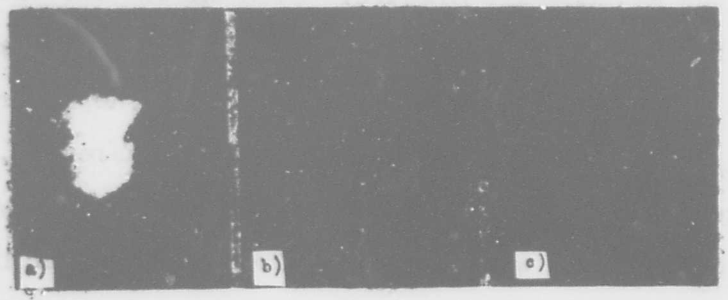

Fig. 10.8. Explosions of freely suspended charge of two cartridges of a safety explosive without a shell; a) in an inert shell, b) and in an active, c) safety shell.

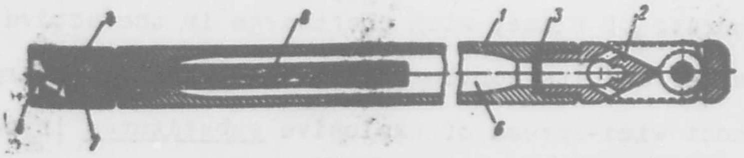

Fig. 10.9. Longitudinal cross-section of cardox cartridge. 1 — steel tube, 2 — discharge head, 3 — steel disk, 4 — ignition head, 5 — valve for filling with carbonic acid, 6 — carbon dioxide, 7 — electrical inputs, 8 — heating composition.

The use of cardox assures high safety with respect to ignition of the methane-air mixture and gives a large yield of large coal lumps, but the destructive action is less, and in many cases insufficient and hence more expensive than the usual safety explosives.

Cardox is used to a limited extent in the coal mines of certain countries. For example, in England the number of explosions set off using cardox in 1953 was about 3% of the total number of explosions.

By its arrangement hydrox is similar to cardox. The basic distinction consists in the fact that, instead of liquid carbon dioxide it contains a charge of powdery composition, capable of low-temperature burning, accompanied by the formation of a significant quantity of gases. This composition includes nearly 55% sodium nitrite, 43% ammonium chloride, and 1.5% magnesium oxide, and forms (by weight) 47% sodium chloride, 30% water vapor and 23% nitrogen. Its advantage over cardox consists in its easier loading.

At last, there have been attempts to apply highly compressed air in place of explosives, but such methods also did not gain wide acceptance.

§ 7. Flame in an Explosion and Shot

1. Flame in an Explosion

As we have seen, the ability of products of explosion to the ignited methane-air and dust-air mixture strongly depends on their temperature. Temperature may be determined by calculation (see Chapter VIII). Calculation, however, gives only the maximum possible value of temperature in the absence of thermal loss and without accomplishment of work by the gases of explosion. The direct experimental determination of the temperature of explosion, as has been noted, is very difficult. In connection with this, for the appraisal of the temperature of products of explosion, as a characteristic of the safety properties of explosives, it has been proposed to use flame of explosion, assuming that the magnitude and duration of this flame is the greater, the higher the temperature.

Magnitude and duration of flame of explosion

The magnitude of the flame is easily determined, by photographing the explosion on stationary film (Fig. 10.10a); the duration of flame may be established by obtaining such a photograph on a film, moving with a definite speed (Fig. 10.10c).

Although in reality, as we will see below, the connection between magnitude and duration of flame, on the one hand, and temperature of explosion, on the other, is more complicated, nevertheless for a long time, attempts were made to quantitatively judge the degree of safety of explosives according to flame characteristics.

Experiments on the determination of the size of the flame of explosion of various explosives were performed by detonation of charges in air at a definite distance from an open camera objective in darkness. The resulting photographs showed that the magnitude of the flame is in accordance with the heat of explosion. Explosives having a large heat of explosion, and consequently, as a rule, higher temperatures of explosion, e.g., fulminating jelly, or gelatin-dynamite, give a very large image of the flame on the photographic plate.

Explosives with comparatively small temperatures of explosion, e.g., safety explosives, give a flame of significantly smaller dimensions. In individual cases, the image of the flame on the photographic plate in general is not in evidence.

Besides the properties of the explosive, the magnitude of the flame is affected by the conditions of the experiment. Thus, for instance, with increasing charge weight, naturally flame size increases as well.

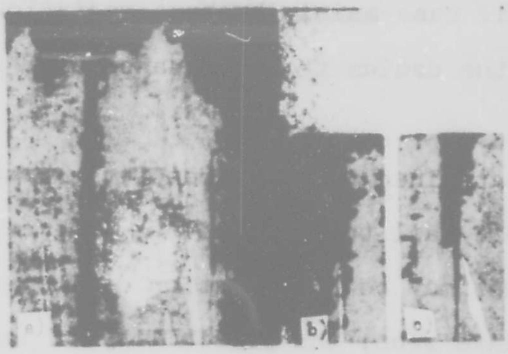

Fig. 10.10. Photograph of explosion gelatin-dynamite. a) on stationary plate; b) on stationary film with slit; c) on moving film.

In certain cases, however, conformity between the heat of explosion and magnitude of flame is not observed. Thus, black powder with a relatively low heat of explosion will form a large flame. This is explained by the fact that black powder does not detonate, and only burns at great speed; the chemical reaction proceeds comparatively slowly and the flame has large dimensions and duration. As a result, black powder turns out to be one of the most dangerous explosives as regards the ignition of gas- and dust-air mixtures.

The example of black powder shows that the duration of the flame is determined not only by the theoretical temperature of explosion, attainable with the use of all of the heat of reaction in the heating of its products, but also by character of flow of the chemical transformation. In detonational transformation gases are formed under high pressure; correspondingly, they expand rapidly and are cooled, especially if work is accomplished in expansion. If however, we are dealing with explosive which detonate slowly (large thickness of reaction zone), and especially with explosives not detonating, but rather burning, then the cooling of gases occurs more slowly.

It is caused in this case mainly by heat radiation, especially if the resistance of the medium to the expansion of gases is insignificant.

The actually attained temperature of the products of transformation may therefore fail to correspond to the calculated temperature; also different may be the duration of its existence. At the same time, as we have seen, the possibility of igniting the methane-air mixture is determined not only by the temperature to which it is heated, but in strong degree by the duration of this temperature. Therefore in the evaluation of the thermal influence of products of explosion on surrounding atmosphere, it is important to know both the temperature of these products, and the duration of action of this temperature. These characteristics were evaluated from the magnitude and duration of the flame in an explosion under certain conditions.

Of the different methods, which have been used for this purpose, we will describe two.

1. According to Mettegang, explosives (100 g) are detonated in a steel mortar. The flame of the explosion is photographed with the aid of a quartz lens (permeable by ultraviolet beams) on photographic film, fixed on a rapidly-rotating drum. Between the lens and drum is placed a screen, having slit, whose direction coincides with the direction of the drum axis. With a motionless drum the height of the image corresponds to the length of the flame, and the width to the width of slot. With rotation of the drum, it is possible from the extent of the image to calculate the duration of the flame, perceived by the photographic film.

2. In the method proposed by Brunswig, the photographic film is motionless; in front of it there revolves an aluminum disk, having a number of slots. The width of the image of the slots on the film serves as a measure of duration of the flame. Simultaneously there is produced a photograph of the flame on motionless film, which allows measurement of the magnitude of the flame (Fig. 10.11).

On the basis of results obtained under certain identical conditions, with respect to duration of the flame, explosives could be divided into three groups:

1. Substances, forming large and prolonged (to 0.25 sec) flame. To this group belong black powder, nitroglycerine, and fulminating jelly, i.e., explosives dangerous with respect to gas and dust.

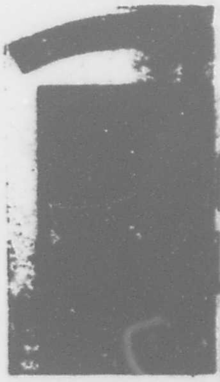

Fig. 10.11. Photograph of explosive flame produced by Brunswig's method.

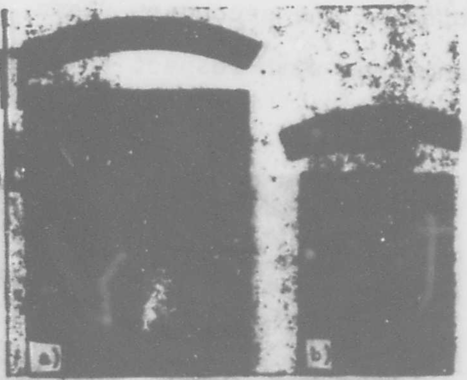

Fig. 10.12. Photographs of flames of various explosives. a) fulminating jelly; b) safety explosive.

2. Substances which generate a flame of small magnitude, the duration of which is below 0.002 sec. To the second group belong the safety explosives (Fig. 10.12).

3. Substances which form a double flame (Fig. 10.13). After a small and brief primary flame, appearing on the plate directly for mouth of mortar, there appears a significantly larger, remote from the mouth, secondary flame, separated from the primary flame by a dark interval. The secondary flame appears as the result of the ignition of combustible gasiform products of explosion after their mixing with air. The secondary flame is produced only by explosives with a strongly negative oxygen balance (for instance, picric acid or trotyl), forming in an explosion much carbon monoxide, hydorgen, and methane. The addition to such explosives of flame extinguishers, e.g., 5% sodium chloride, removes the secondary flame (Fig. 10.13c). The duration of the secondary flame is comparatively great. For picric acid it constitutes nearly 0.01 sec; the interval of time between primary and secondary flame is nearly 0.001 sec. Due to the great duration of the secondary flame, the explosives which form it are very dangerous with respect to both gas and dust.

Fig. 10.13. Photograph of double flame in an explosion of picric acid and trotyl.
a) picric acid; b) trotyl; c) picric acid with 5% sodium chloride.

Subsequently it was clarified, that the magnitude of the flame, fixed photographically, depends likewise on the conditions of detonation. In certain cases, less dangerous safety explosives and conditions of detonation can give large flame and vice-versa. Therefore, the flame of explosion of charge in a mortar-groove cannot serve as a characteristic of the comparative safety of different safety explosives and methods of detonation.

The glow appearing in an explosion, can, however, provide a correct characteristic of the danger of tested explosives, if method of evaluation of this glow is carried in conformity with contemporary theoretical notions about the causes and mechanism of ignition of gas in explosions. This, during tests in the mortar-groove (see p. 721), it turned out that those explosives, which give on the photographs a significant glow in the groove and especially at the reflecting wall, ignite gases more easily. Especially sharp is the resulting distinction in the dimensions of zone of glow and its intensity in the comparison of unsafe and safety explosives.

However, a distinction can also be established between safety explosives, differing in degree of danger (size of limiting charge in mortar-groove). On Fig. 10.14 are given photographs of glow during explosions of the charges of two explosives. The first of them (upper photograph) ignited the methane-air mixture by the explosion of a charge of 10 cartridges; the second explosive did not ignite the gas with a charge of 16 cartridges — the maximum, which could be fitted in the groove. Let us add that the brisance of the second explosive was even somewhat higher than that of the first, so that distinction in intensity of glow could not be explained by the different intensities of shock waves, but was apparently, caused by burning of the products of explosion upon braking at the wall.

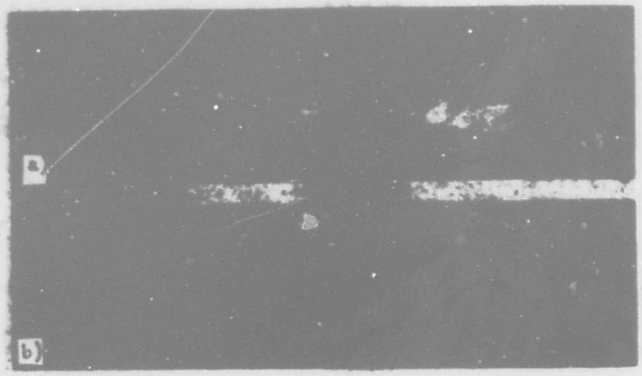

Fig. 10.14. Photograph of explosion in mortar-groove of two safety explosives.

A large influence on the character of glow is exerted by the distribution of reactive component (liquid explosive) in an inert salt; that distribution, which leads to a strong and prolonged glow, is simultaneously dangerous with respect to the ignition of the methane-air mixture as well.

Ambient effect on glow in an explosion

The light phenomena observed in explosions until recently were considered caused solely by the glow of products of explosion of solid (if they are formed) and gaseous products, heated at the expense of the heat of explosion to a high temperature. The work of the French researchers Mürauer and Michel-Levy showed that radiation of the products explosion is not the only, and often not the basic source of glow in an explosion.

Mürauer established a strong dependence of the intensity of glow on properties of the gas, in whose atmosphere the charge is detonated. Experiments were performed in the following way: small lumps of lead azide were placed at a small distance from each other on a piece of glass along the sides of an isosceles triangle. The lump, located at the summit (between equal sides), was detonated by heating it with an incandescent wire. The detonation was transmitted from one lump to another. In the middle of base of the triangle, shock waves met. The glass with the azide placed under a glass bell with flat cover, through light phenomena were photographed. The bell was filled with different gases — argon, nitrogen, carbon dioxide, butane, etc. (Fig. 10.15). It turned out that the intensity of glow in an explosion very strongly depends on the nature of gas surrounding the explosive. The strongest glow is given by the gas with the minimum heat capacity — argon; after it follow nitrogen, carbon dioxide, and, at last, butane, which has the maximum heat capacity.

Further experiments showed that intensity of glow depends, apparently, not only on heat capacity, but also on the density of the gas. An increase in pressure decreases the intensity of light phenomena in all gases (Fig. 10.16).

The duration of glow in the experiments of Mürauer was extremely small, with a charge of 0.4 g, the explosive (in this experiment he used tetranitromethane with toluene) is less than $5 \cdot 10^{-6}$ sec. The brightness of the glow is very great. According to trial experiments and the calculations of Mürauer, it exceeds the brightness of sunlight.

It seemed natural to ascribe the glow to gasiform products of detonation having a high temperature. In this case, however, the dependence of glow on the nature of the surrounding gas would remain uncomprehensible. Furthermore, on the glass it was possible to detect after the explosion around the place occupied by the azide lump a deposition of lead, more or less uniform in all directions

(Fig. 10.17). A sharp strengthening of these deposits is observed only approximately at the mid-points between the lumps, where the particle of the products of explosion of neighboring lumps meet. The maximum glow on photographs corresponds, however, not in this zone, but to the zone, directly adjacent to a "passive" lump, and besides this, has definite directedness (Fig. 10.18). Furthermore, in gases with a large heat capacity, glow disappears directly at the surface of the transmitting lumps of azide.

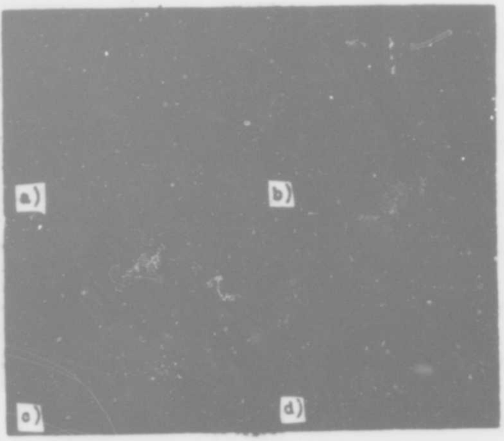

Fig. 10.15. Glow during lead azide explosion in various gases. a) in argon; b) in nitrogen; c) in carbon dioxide; d) in butane.

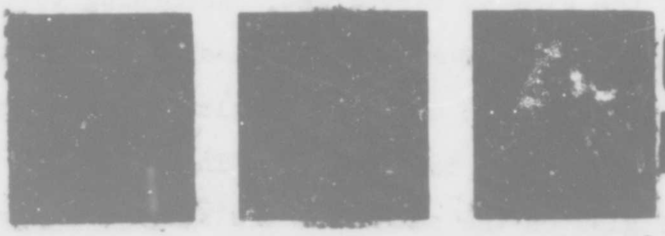

Fig. 10.16. Dependence of intensity of glow in explosion of lead azide on pressure of surrounding gas.

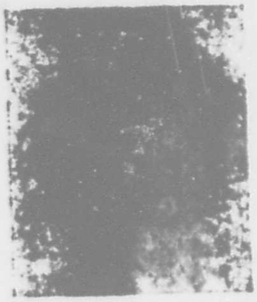

Fig. 10.17. Lead deposits after explosion of chain of lumps of lead azide on glass.

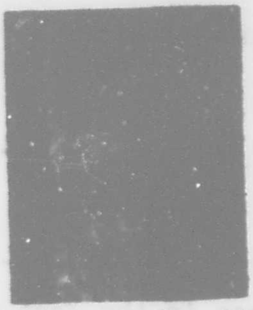

Fig. 10.18. Glow in explosion of a chain of lumps of lead azide.

Finally, if the glow were emitted by gases of explosion, then one should have expected a strong dependence of the intensity of glow on the temperature of explosion. Experiments with mixtures tetranitromethane and toluene with different temperature of explosion (6000°C and 4500°C), but with approximately identical brisance did not exhibit a noticeable distinction in the intensity of glow.

All of this is very difficult to correlate with the assumption that the glow emanates from the gasiform products of explosion as such, or in mixture with the surrounding gas. Therefore, as the cause of glow one should consider the shock wave that heats the gas, through which it passes, to very high temperature.

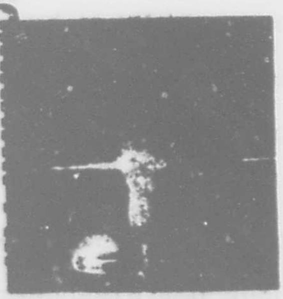

Fig. 10.19. Glow during reflection of shock wave from freely suspended sheet of paper.

Calculations show that if in air at atmospheric pressure, there propagates a shock wave with jump of pressure on front of just 400 atm (tech.), then in the zone of compression there may be attained a temperature of 10,500°C; for argon with those same conditions calculations give 27,000°C. Of course, these figures are strongly exaggerated, since they were calculated under the assumption of the absence during the passage of the wave of any change in the medium, accompanied by the absorption of heat. Actually, there undoubtedly occurs a dissociation of polyatomic molecules into atoms and intense ionization, which determines the observed glow.

Indirect proof of the excitation of glow by the shock wave Mürauer sees in the fact that the spectra of glows, obtained in the explosion of explosives with additives of explosive metallic salts, do not differ from the spectra, obtained in absence of such salts, and do not reveal a single line of the spectrum of the introduced metal. If, however, the metal is introduced into the gas surrounding the explosive, then in the flame of explosion are observed the line spectra of the corresponding metals, extending far into the ultraviolet region.

The glow of explosion is especially strengthened if there occurs an encounter of the shock waves; it appears also and in the reflection of the shock wave even from a very light object such as a sheet of paper (Fig. 10.19), thread, etc.

According to Mürauer, the flame and shock wave are related by following mechanism. If the intensity of the shock wave is sufficiently great, then the air, surrounding the explosive, is adiabatically compressed in front of the wave, and, being heated to a high temperature, glows brightly. This is precisely the flame of explosion. After the passage of shock wave, the glow does not disappear immediately. Thus, after the shock wave follows luminescent air moving with great speed and not having anything in common with the gasiform products of explosion, which are opaque and weakly luminescent, and which travel with a relatively low speed.

At a certain distance from the boundary of the charge, the intensity of the shock wave drops to such a degree that it ceases to produce glow, but the activated gases for a certain time follow it with gradually decreasing intensity of glow.

Mürauer supposes, that even that glow, which is fixed in the photographing of an explosion, for instance in a Trauzl bomb, has as its cause not the luminescent products of explosion, but shock wave, and depends mainly on the brisance of the explosive. Indeed, the corresponding experiments with various explosives showed, that glow disappears in butane and very intensely in argon.

2. Muzzle Flame in Firing of a Shot

In firing, especially from high-caliber weapons, in addition to the poorly noticeable flame directly at the weapon muzzle associated with the glow of products of burning of powder, there is observed the formation of a large flame at a certain distance from the muzzle. This flame will be called muzzle flame. The formation of the muzzle flame is undesirable, because it reveals, especially during firing at night or in foggy weather, the location of the weapon and, furthermore, blinds the artillery men, performing the firing. The muzzle flame is formed in the same way, as the secondary flame, in the explosion of an explosive with a negative oxygen balance.

The gasiform products of burning of powder, containing significant amounts (up to 60%) of hydrogen, carbon monoxide, and methane, mix with air, to form a combustible mixture. Inasmuch as powder gases ejected into the atmosphere are still very hot, the temperature of this mixture may be above its flash temperature; in this case ignition occurs. The proof of this mechanism of formation of the muzzle flame is, in the first place, the fact that the flame appears only at a certain distance from the muzzle after there occurs the mixing of gases with air; this takes place not in the center of the gas cloud but in its frontal part; and secondly, the absence of the muzzle flame during firing in a atmosphere of nitrogen or carbon dioxide.

Mechanical and chemical methods are used for the elimination of the muzzle flame. The former consist in the use of various kinds of muzzle attachments and other nozzles, assuring the cooling of powder gases emerging from the barrel, before they mix with air. Chemical methods consist in the introduction into the powder charge of special additives, called flame extinguishers. The basic purpose of these additives consists in lowering, the temperature of burning of the powder, and therefore the temperature of the powder gases, emerging in firing from the bore of the weapon, and thus hampering their ignition. These additives are substances with a large content of combustible elements, e.g., vaseline, rosin, centralite, dibutylphthalate, and camphor, which decrease the content of oxygen in the powder and correspondingly the temperature of burning. In principle it would have been also possible to use additions, increasing the oxygen balance, which would decrease the content of combustible gases in the products of burning. However, this way of combatting the muzzle flame has not received practical application.

Flame extinguishing additives are also used in the form of additional charges placed ahead of the powder charge. In such a form are used mainly salts of potassium — potassium chloride, potassium sulfate, acid potassium oxalate, etc. The action of these salts is in significant measure not only of a thermal nature. Potassium salts in high measure possess the ability to break the chain of reactions of ignition of carbon monoxide and hydrogen. This effect, obviously, determines in significant measure the flame extinguishing action of such additives, employed in quantities, not exceeding several percents of the weight of the powder.

3. Flareback

After firing with smokeless powder, sometimes upon opening of the lock of the weapon there is formed a flame, emerging from the rear part of the barrel, which has been called flareback. It is especially dangerous in tank, self-propelled and casemate weapons. Flareback is associated with the ignition of combustible products of powder burning, remaining after firing in the bore of the weapon. Upon opening of the lock, these gases, mixing with air, form an explosive mixture. The temperature of the powder up to the moment of opening of the lock usually has time to drop significantly. Correspondingly, the temperature of the resulting gas-air mixture is too low to produce ignition. The mixture, can, however, ignite from the smoldering residue of the cap fabric or cords by which the powder bundles were joined if they did not burn completely in firing. Therefore, flareback appears especially frequently in firing from high-caliber weapons, using cartridge-type loading. In case-loaded weapons, flareback is observed with very fast firing. The appearance of flareback is most dangerous at the instant of introduction into the chamber of a new charge, which can ignite prior to the shutting of the lock and damage the weapon.

The formation flareback is assisted by low density of loading, and also small charge weight; in both cases more combustible gases will form. Nitroglycerine powders, whose products of burning contain more carbon dioxide in comparison with pyroxylin powders, are less inclined to produce flareback. One of the methods of combatting flareback consists in the application of caps made of nitrified fabric, which burns up completely in firing without leaving a smoldering residue, and also in the use of various kinds of flash extinguishers. Such flash extinguishers are, in particular, products of burning black powder; therefore, the use of igniters of black powder decreases the probability of the appearance of flareback.

The latest investigations have shown that the cause for the formation of flareback may also be the "leakage" of the muzzle flame into the gun bore. Therefore, the prevention of muzzle flame formation, or at least its leakage into the bore is one of methods of prevention of flareback.

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Chapter V

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APPENDICES

A P P E N D I X 1

LIMITS OF COMBUSTIBILITY OF MIXTURES OF GASES AND VAPORS WITH AIR

Substance	Formula	Limits of combustibility (in % combustible gas by volume)	
		Lower	Upper
Paraffins			
Methane	CH_4	5,00	15,00
Ethane	C_2H_6	3,00	12,50
Propane	C_3H_8	2,12	9,35
Butane	C_4H_{10}	1,86	8,41
Isobutane	C_4H_{10}	1,80	8,44
Pentane	C_5H_{12}	1,40	7,80
Isopentane	C_5H_{12}	1,32	—
2.2-Dimethylpropane	C_5H_{12}	1,38	7,50
Hexane	C_6H_{14}	1,18	7,40
Heptane	C_7H_{16}	1,10	6,70
2.3-dimethylpentane	C_7H_{16}	1,12	6,75
Octane	C_8H_{18}	0,95	—
Nonane	C_9H_{20}	0,83	—
Decane	$C_{10}H_{22}$	0,77	5,35
Olefins			
Ethylene	C_2H_4	2,75	28,60
Propylene	C_3H_6	2,00	11,10
Butene-1	C_4H_8	1,65	9,95
Butene-2	C_4H_8	1,75	9,70
Amylene	C_5H_{10}	1,42	8,70
Acetylenes			
Acetylene	C_2H_2	2,50	80,00
Aromatic hydrocarbons			
Benzene	C_6H_6	1,40	7,10
Toluene	C_7H_8	1,27	6,75
o-Xylol	C_8H_{10}	1,00	6,00

Appendix 1 continued

Substance	Formula	Limits of combustibility (in % combustible gas by volume)	
		Lower	Upper
Cyclical Hydrocarbons			
Cyclopropane	C_3H_6	2,40	10,40
Cyclohexane	C_6H_{12}	1,26	7,76
Methylcyclohexane	C_7H_{14}	1,15	—
Terpenes			
Turpentine	$C_{10}H_{16}$	0,80	—
Alcohols			
Methyl alcohol	CH_4O	6,72	36,50
Ethyl alcohol	C_2H_6O	3,28	18,95
Allyl alcohol	C_3H_6O	2,50	18,00
n-Propyl alcohol	C_3H_8O	2,15	13,50
Isopropyl alcohol	C_3H_8O	2,02	11,80
n-Butyl alcohol	$C_4H_{10}O$	1,45	11,25
Isobutyl alcohol	$C_4H_{10}O$	1,68	—
Amyl alcohol	$C_5H_{12}O$	1,19	—
Isoamyl alcohol	$C_5H_{12}O$	1,20	—
Aldehydes			
Acetaldehyde	C_2H_4O	3,97	57,00
Crotonaldehyde	C_4H_6O	2,12	15,50
Furfurole	$C_5H_4O_2$	2,10	—
Paraldehyde	$C_6H_{12}O_3$	1,30	—
Ethers			
Methylethyl ether	C_3H_8O	2,00	10,00
Diethyl ether	$C_4H_{10}O$	1,85	36,50
Divinyl ether	C_4H_6O	1,70	27,00
Ketones			
Acetone	C_3H_6O	2,55	12,80
Methylethylketone	C_4H_8O	1,81	9,50
Methylpropylketone	$C_5H_{10}O$	1,55	8,15
Methylbutylketone	$C_6H_{12}O$	1,35	7,60
Acids			
Acetic acid	$C_2H_4O_2$	5,40	—
Prussic acid	HCN	5,60	40,00
Esters			
Methylformate	$C_2H_4O_2$	5,05	22,70
Ethylformiate	$C_3H_6O_2$	2,75	16,40
Methyl acetate	$C_3H_6O_2$	3,15	15,60
Ethyl acetate	$C_4H_8O_2$	2,18	11,40
Propylacetate	$C_5H_{10}O_2$	1,77	8,00
Isopropylacetate	$C_5H_{10}O_2$	1,78	7,80
Butylacetate	$C_6H_{12}O_2$	1,39	7,55
Amylacetate	$C_7H_{14}O_2$	1,10	—
Hydrogen			
Hydrogen	H_2	4,00	74,20

Appendix 1 continued

Substance	Formula	Limits of combustibility (in % combustible gas by volume)	
		Lower	Upper
Compounds of nitrogen			
Ammonia	NH_3	15,50	27,00
Cyanogen	C_2N_2	6,60	42,60
Pyridine	C_5H_5N	1,81	12,40
Ethylintrate	$C_2H_5NO_3$	3,80	—
Ethylinitrite	$C_2H_5NO_2$	3,01	50,00
Oxides			
Carbon monoxide	CO	12,50	74,20
Ethylene oxide	C_2H_4O	3,00	80,00
Propylene oxide	C_3H_6O	2,00	22,00
Dioxane	$C_4H_8O_2$	1,97	22,25
Diethylperoxide	$C_4H_{10}O_2$	2,34	—
Sulfides			
Carbon bisulfide	CS_2	1,25	50,00
Hydrogen sulfide	H_2S	4,30	45,50
Carbon oxysulfide	COS	11,90	28,50
Chlorides			
Methylchloride	CH_3Cl	8,25	18,70
Ethylchloride	C_2H_5Cl	4,00	14,80
Propylchloride	C_3H_7Cl	2,60	11,10
Butylchloride	C_4H_9Cl.	1,85	10,10
Izobutylchloride	C_4H_9Cl	2,05	8,75
Allylchloride	C_3H_5Cl	3,28	11,15
Amylchloride	$C_5H_{11}Cl$	1,60	8,63
Vinylchloride	C_2H_3Cl	4,00	21,70
Ethylenechloride	$C_2H_4Cl_2$	6,20	15,90
Propylenechloride	$C_3H_6Cl_2$	3,40	14,50
Bromides			
Methylbromide	CH_3Br	13,50	14,50
Ethylbromide	C_2H_5Br	6,75	11,25
Allybromide	C_3H_5Br	4,36	7,25
Amines			
Methylamine	CH_5N	4,95	20,75
Ethylamine	C_2H_7N	3,55	13,95
Dimethylamine	C_2H_7N	2,80	14,40
Propylamine	C_3H_9N	2,01	10,35
Diethylamine	$C_4H_{11}N$	1,77	10,10
Trimethylamine	C_3H_9N	2,00	11,60
Triethylamine	$C_6H_{15}N$	1,25	7,90

APPENDIX 2

LIMITS OF COMBUSTIBILITY OF MIXTURES OF GASES AND VAPORS WITH OXYGEN

Substance	Formula	Limits of combustibility (in % combustible gas by volume)	
		Lower	Upper
Hydrogen	H_2	4.65	93,9
Deuterium	D_2	5.00	95,0
Carbon monoxide	CO	15,50	93,9
Methane	CH_4	5.40	59,2
Ethane	C_2H_6	4.10	50,5
Ethylene	C_2H_4	2,90	79,9
Propylene	C_3H_6	2.10	52,8
Cyclopropane	C_3H_6	2.45	63,1
Ammonia	NH_3	13.50	79,0
Diethyl ether	$C_4H_{10}O$	2.10	82,0
Divinyl ether	C_4H_6O	1.85	85,5

Note: The limits of combustibility are determined at atmospheric pressure and room temperature (due to the low elasticity of certain vapors their upper limits are determined for somewhat higher temperatures) for propagation of flame from bottom to top in a tube or bomb by 50 mm or more in diameter.

A P P E N D I X 3

SENSITIVITY OF EXPLOSIVES TO IMPACT*

Sensitivity is expressed as the minimum energy of impact in kgm, at which there is observed at least one explosion in six parallel experiments. Determinations were performed for impact between two steel rollers 15 mm in diameter and 10 mm in diameter and for impact between a steel roller and a steel plate of dimensions 20 × 20 × 5 mm having incision, as in a file.

Explosive	Size of particles мм	Sensitivity in kgm with impact determ.ned						
		between steel rollers Ø 15 X 15 and Ø 10 X 10 mm			on plates with incision 20 X 20 X 5 mm with roller Ø 10 X X 10 mm			
		Weight of load in kg						
		5	1	0,1	5	1	0,1	0,025
1	2	3	4	5	6	7	8	9
Potassium chlorate red phosphorus 75/25	0,06—0,075			0.003				[illegible]
Silver acetylide (from nitric acid solution)	<0,001	1	0,5					[illegible]
Mercury acetylide	Fine-grained			0,06				[illegible]
Cyanurtriazide	0,02—0,55			0,04				[illegible]
Silver acetylide (from neutral solution)		1	0,2					[illegible]
Silver acetylide (from ammonium solution)	0,01		0,1	0,08				[illegible]

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*From data of Kennen, Ide, and Haupt, Explosivstoffe, 6, 232 (1958).

Appendix 3 continued

Explosive	Size of particles мм	Sensitivity in kgm with impact determined						
		between steel rollers Ø 15 X 15 and Ø 10 X 10 mm			on plates with incision 20 X 20 X 5 mm with roller Ø 10 X X 10 mm			
		Weight of load in kg						
		5	1	0,1	5	1	0,1	0,025
1	2	3	4	5	6	7	8	9
Lead azide	0,01—0,1							0,003
Cuprous acetylide								0,003
Tricycloacetone peroxide	<0,07			0,01				0,003
Mercury azide H_gN_3	Grainy			0,03				0,003
Hexamethylenetriperoxide-diamine	<0,1			0,01				0,003
Lead trinitroresorcinate	0,05—0,2	1,5						0,005
White mercury fulminate	0,05—0,8							0,005
Tetrazene	0,003—0,1	1	0,6					0,005
Grey mercury fulminate	0,05—0,8			0,06				0,005
Mercuric oxalate	0,06—0,5	2					0,02	0,008
Eritritetranitrate	0,1—0,5	0,5	0,2				0,03	0,02
PETN	0,1—0,5	0,5	0,2				0,05	0,02
Azoisobutyric nitrile acid	0,1—0,2	0,5	0,2		0,5	0,2		
Chloratite 1**	Fine-grained				0,5	0,2		
Tetryl	<0,3	2,5	0,5		0,5	0,2		
Nitrocellulose 13.4%N	Fine-fibre	0,5	0,3			0,2		
Colloxylin 12.2%N	Fine-fibre	0,5	0,4		1	0,2		
Potassium hexanitro-diphenylamine	0,1—0,5	0,5	0,2		0,5	0,3		
Ammongelite 1***	Gelatinous		0,1*		0,5	0,4		
Ammongelite 3****	Gelatinous				1	0,4		
Hexogene	0,1—0,5	1	0,3			0,4	0,1	
Trinitrobenzoic acid	<0,2	1			1	0,4		

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*Values obtained between steel rollers ϕ 10 × 10 mm, in casing.

**Chloratite 1 consists of $KCLO_3$ (88.5%), wood meal (8.5%), and paraffin oil (3%).

***Ammongelite 1 consists of ammonium nitrate (52.3%), nitroglycol (37.7%), trinitrotoluene (4%), collodion cotton (1.8%), wood meal (4%), and mummy (0.2%).

****Ammongelite 3 consists of ammonium nitrate (55%) diglycoldinitrate (22%), trinitrotoluene (5%) and dinitrotoluene (6%).

Appendix 3 continued

Explosive	Size of particles мм	Sensitivity in kgm with impact determined						
		between steel rollers Ø 15 X 15 and Ø 10 X 10 mm			on plates with incision 20 X 20 X 5 mm with roller Ø 10 X 10 mm			
		Weight of load in kg						
		5	1	0,1	5	1	0,1	0,025
1	2	3	4	5	6	7	8	9
Donarite 1**	Fine-grained	1	0.6		1,5	0,4		
Sodium dinitroorthocresolate	0,1—0,5	0,5	0,5		0,5	0,4		
Nitroglycerine				0,03*	0,5	0,5		
Trinitroresorcin	0,1—0,5	1			0,5	0,5		
Hexanitrodiphenylamine	0,06—0,2	1	0,8		0,5	0,5		
Nitroglycol				0,05*	1	0,5		
Picric acid	0,1—2,0	5			1	0,5		
Calcium azide	0,1—0,5	5			2	0,6		
Strontium azide	0,1—0,5	3			2	0,6		
Barium azide	0,1—0,5	1			1,5	0,8		
Ammonium bichromate	0,1—0,5	1,5			1	0,8		
Powder pulp (75% KNO_3)	<0,5	1,5			1	1		
Dinitrosopentamethylenetetramine	0,06—0,3	1			1			
Ammonium perchlorate	0,1—0,5	1,5			1			
Tetranitrocarbazole	0,1—0,5	1			1			
Ethylenediamine-dinitrate	0,1—0,5	1,5			1			
Trinitronapthalene	0,1—0,5	1,5			1,5			
Ammonium dinitroorthocresolate	<0,2	1,5			1,5			
Pyrotechnic composition***	0,5—1,0	2			1,5			
Mercuric oxycyanide	0,1—0,5	2			1,5			
Sodium paranitrophenolate (anhydrous)	0,06—0,2	2			2			
Trinitroaniline	0,1—0,5				2,5			
Silver oxalate	<0,2	5			4			

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*Values obtained between steel rollers ϕ 10 × 10 mm in closing.

**Donarite 1 contains ammonium nitrate (80%), aromatic nitro compounds (14%) and nitroglycerine (4%).

***Pyrotechnic composition contains barium nitrate (52%), iron filings (30%), dextrine (9%) and aluminum (7%).

APPENDIX 4

OXYGEN BALANCE OF CERTAIN EXPLOSIVE SUBSTANCES AND COMPONENTS OF EXPLOSIVE MIXTURES

Substance	Formula	Atomic or molecular weight	Oxygen balance %
Aluminum	Al	27	—89,0
Ammonium carbonate	$(NH_4)_2CO_3$	96	—32,2
Ammonium nitrate	NH_4NO_3	80	+20,0
Ammonium oxalate	$(NH_4)_2C_2O_4 \cdot H_2O$	142	—45,1
Ammonium perchlorate	NH_4ClO_4	117,5	+34,0
Ammonium picrate	$NH_4C_6H_2(NO_2)_3O$	246	—52,0
Ammonium sulfate	$(NH_4)_2SO_4$	132	—36,4
Ammonium chloride	NH_4Cl	53,5	—44,9
Anthracene	$C_{14}H_{10}$	178	—296,6
Barium nitrate	$Ba(NO_3)_2$	261	+30,6
Barium chlorate	$Ba(ClO_3)_2 \cdot H_2O$	322	+29,8
Barium chromate	$BaCrO_4$	253,5	+9,5
Barium peroxide	BaO_2	169,37	+9,4
Barium silicide	$BaSi_2$	194	—41,2
Beryllium	Be	9	—177,5
Paper(cartridge shells)	—	—	—120,0
Vaseline	$C_{18}H_{38}$	254	—347,0
Hexanitrodiphenylamin	$[C_6H_2(NO_2)_3]_2NH$	439	—52,8
Hexogene	$C_3H_6N_6O_6$	222	—21,6
Glycerine	$C_3H_5(OH)_3$	92	—122,8
Glucose	$C_6H_{12}O_6$	180	—106,5
Mercury fulminate	$Hg(CNO)_2$	284	—11,3
Dextrin	$C_6H_{10}O_5$	162	—118,5
Dinitrobenzene	$C_6H_4(NO_2)_2$	168	—95,3
Dinitroglycerine	$C_3H_5(ONO_2)_2OH$	166	—20,3
Dinitroxylene	$C_6H_2(NO_2)_2(CH_3)_2$	196	—130,5
Dinitronapthalene	$C_{10}H_6(NO_2)_2$	218	—139,4
Dinitrochlorohydrin	$C_3H_5(ONO_2)_2Cl$	200,5	—16,0
Dinitrophenol	$C_6H_3(NO_2)_2OH$	184	—78,2

Appendix 4 continued

Substance	Formula	Atomic or molecular weight	Oxygen balance %
Dinitrotoluene	$C_6H_3(NO_2)_2CH_3$	182	−114,4
Dicyandiamide	$(CN)_2(NH_2)_2$	84	−114,3
Potassium bichromate	$K_2Cr_2O_7$	295	+16,3
Potassium nitrate	KNO_3	101	+39,6
Potassium chlorate	$KClO_3$	122,5	+39,2
Potassium perchlorate	$KClO_4$	138,5	+46,2
Potassium picrate	$C_6H_2(NO_2)_3OK$	267	−36,9
Calcium nitrate	$Ca(NO_3)_2 \cdot 4H_2O$	236	+33,9
Calcium perchlorate	$Ca(ClO_4)_2$	239	+53,6
Calcium chlorate	$Ca(ClO_3)_2$	207	+46,4
Calcium silicide	$CaSi_2$	96	−83,3
Camphor	$C_{10}H_{16}O$	152	−284,2
Kerosene	—	—	−343,0
Cellulose	$C_6H_{10}O_5$	162	−118,5
Starch	$C_6H_{10}O_5$	162	−118,5
Magnesium	Mg	24,3	−65,8
Mannite	$C_6H_8(OH)_6$	182	−114,3
Mononitroglycerine	$C_3H_5(ONO_2)(OH)_2$	137	−52,6
Mononitronaphthalene	$C_{10}H_7NO_2$	173	−198,8
Mononitrochlorohydrin	$C_3H_5(ONO_2)OHCl$	155,5	−48,8
Mononitrotoluene	$C_6H_4(NO_2)CH_3$	137	−181,0
Mononitrophenol	$C_6H_4(NO_2)OH$	139	−132,4
Cereal flour	$C_{15}H_{25}O_{11}$	381	−132,0
Wood meal (purified)	$C_{15}H_{22}O_{10}$	362	−137,0
Wood meal (sawdust)	—	—	−135,0
Vegetable oil	$C_{23}H_{36}O_7$	424	−215,0
Sodium nitrate	$NaNO_3$	85	+47,0
Sodium chlorate	$NaClO_3$	106,5	+45,0
Sodium perchlorate	$NaClO_4$	122,5	+52,2
Sodium picrate	$C_6H_2(NO_2)_3ONa$	251	−41,4
Napthalene	$C_{10}H_8$	128	−300,0
Nitrobenzene	$C_6H_5NO_2$	123	−162,7
Nitroglycerine	$C_3H_5(ONO_2)_3$	227	+3,5
Nitroguanidine	$CN_4H_4O_2$	104	−30,8
Nitropolyglycerine	—	—	+2,0
Nitrocellulose (collodional)	$C_{24}H_{31}N_9O_{38}$	1053	−38,7
Nitrocellulose (pyroxylin)	$C_{24}H_{29}N_{11}O_{42}$	1143	−28,6
Nitro starch	—	—	−33,5
Nitromannite	$C_6H_8(NO_3)_6$	452	+7,1
Octogene	$C_4H_8N_8O_8$	296	−21,6
Paraffin	$C_{24}H_{50}$	338,52	−346,0
Hydrogen peroxide	H_2O_2	34	+47,0
Picric acid	$C_6H_2(NO_2)_3OH$	229	−45,4

Appendix 4 continued

Substance	Formula	Atomic or molecular weight	Oxygen balance %
Cane sugar	$C_{12}H_{22}O_{11}$	342	—112,2
Sulfur	S	32	—100,0
Lead nitrate	$Pb(NO_3)_2$	331	+24,2
Turpentine	$C_{10}H_{16}$	136	—329,4
Strontium nitrate	$Sr(NO_3)_2$	211,5	+37,8
Antimony sulfide	Sb_2S_3	336	—42,9
Metallic antimony	Sb	120	—20,0
Tannin	$C_{14}H_{10}O_9$	322	—119,3
Tetranitroaniline	$C_6H(NH_2)(NO_2)_4$	273	—32,2
Tetranitrodiglycerine	$(C_3H_5)_2O(NO_3)_4$	346	—18,5
Tetranitrodimethylaniline	$C_6H(NO_2)_4N(CH_3)_2$	301	—61,2
Tetranitromethane	$C(NO_2)_4$	196	+49,0
Tetranitronaphthalene	$C_{10}H_4(NO_2)_4$	308	—72,7
Tetryl	$C_6H_2(NO_2)_4NCH_3$	287	—47,4
Trinitro analine	$C_6H_2(NO_2)_3NH_2$	228	—56,6
Trinitrobenzene	$C_6H_3(NO_2)_3$	213	—56,3
Trinitrodimethyl aniline	$C_6H_2(NO_2)_3N(CH_3)_2$	256	—87,5
Trinitrocresol	$C_6H\cdot CH_3(NO_2)_3OH$	243	—62,6
Trinitronaphthalene	$C_{10}H_5(NO_2)_3$	263	—100,4
Trinitroresorcin	$C_6H(NO_2)_3(OH)_2$	245	—35,9
Trinitrotoluene	$C_6H_2(NO_2)_3CH_3$	227	—74,0
Trotyl oil	—	—	—84,0
Trinitroxylene	$C_6H(NO_2)_3(CH_3)_2$	241	—89,6
PETN	$C(CH_2ONO_2)_4$	316	—10,1
Carbon	C	12	—266,7
Phenol	C_6H_5OH	94	—238,3
Ethylenedinitramine	$C_2H_6N_4O_4$	150	—32,0

APPENDIX 5

HEAT OF FORMATION OF DIFFERENT EXPLOSIVE SUBSTANCES, INITIAL PRODUCTS; COMPONENTS OF EXPLOSIVE MIXTURES AND PRODUCTS OF EXPLOSION[1]

(Diamond was taken as the standard state for carbon)

Substance	Formula	Heat of formation at 18°C and constant pressure, kcal/mole
Ammonium azide[2]	NH_4N_3	−26,79
Barium azide	BaN_6	5,32
Potassium azide	KN_3	−0,33
Calcium azide	CaN_6	−11,03
Lithium azide	LiN_3	−2,58
Azide of copper (oxide)	CuN_3	−67,23
Azide copper (oxidized)	CuN_6	−140,4
Sodium azide	NaN_3	−5,08
Mercury azide (oxide)	Hg_2N_6	−141,5
Rubidium azide	RbN_3	0,07
Lead azide	PbN_6	−115,5
Silver azide	AgN_3	−74,17
Strontium azide	SrN_6	−1,72
Thallium azide	TlN_3	−55,78
Cesium azide	CsN_3	2,37
Azobenzene (trans)	$C_{12}H_{10}N_2$	−71,4
Azobenzene (cis)	$C_{12}H_{10}N_2$	−81,0
Acardite I (asymmetric diphenylcarbamide)	$C_{13}H_{12}ON_2$	32,6

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[1] The data below are based on the tables of Medar [Mèm. Art. franc. Vol. 28, 415 (1954)], supplemented by later data of Medar, Tavernier, and other researchers. Unfortunately, the tables of Medar are not free of inaccuracies and errors which it was impossible to eliminate wholly.

[2] Data for azides refer to 25°.

Appendix 5 continued

Substance	Formula	Heat of formation at 18°C and constant pressure, kcal/mole
Acardite II (N-methyl N'N' diphenylcarbamide)	$C_{14}H_{14}ON_2$	29,1
Acardite III (N-ethyl N'N' diphenylcarbamide)	$C_{15}H_{16}ON_2$	40,5
N-allyl-N'N'-diphenylcarbamide	$C_{16}H_{16}ON_2$	13,48
Ammonia (gas)	NH_3	11,0
Ammonia (solution)	NH_3	19,35
Ammonium alum	$NH_4Al(SO_4)_2 \cdot 12H_2O$	1417,6
Anhydride boric (vitreous)	B_2O_3	281
Anhydride vanadium	V_2O_3	373
Anhydride maleic (solid)	$C_4H_2O_3$	114,1
Anhydride arsenous octahedral	As_2O_3	154,1
Anhydride sulfuric (solid, β-modification)	SO_3	105,2
Anhydride sulfurous (gas)	SO_2	70,92
Anhydride sulfurous (solution)	SO_2	79,5
Anhydride coal (gas)	CO_2	94,51
Anhydride phosphorous (amorphous)	P_2O_3	367,0
Anhydride phthalic (solid)	$C_8H_4O_3$	114,1
Anhydride hypochlorous (gas)	Cl_2O	—18,64
Anhydride hypochlorous (solution)	Cl_2O	—9,90
Anhydride chromium	CrO_3	137,1
Anhydroenneageptite	$C_9H_{18}O_6$	307,0
Anisole	C_7H_8O	30,2
Aniline (liquid)	C_6H_7N	—4,5
Anthracene (solid)	$C_{14}H_{10}$	—24,2
N-Acetyldiphenylamine	$C_{13}H_{13}ON$	13,99
N-Acetylhexahydrodiphenylamine	$C_{14}H_{19}ON$	75,80
Acetylene (gas)	C_2H_2	—53,3
Silver acetylide	Ag_2C_2	—83,6
Acetylenedicarbamide	$C_4H_6O_2N_4$	118,63
Acetoacetydiphenylamine	$C_{16}H_{15}O_2N$	58,57
Acetone (liquid)	C_3H_6O	60,9
Acetonitrile (liquid)	C_2H_3N	—12,9
Benzalacetone (solid)	$C_{10}H_{10}O$	28,3
Benzaldehyde	C_7H_6O	21,5
Benzildiphenylamine	$C_{20}H_{17}N$	—30,14
Benzene (liquid)	C_6H_6	—8,3

Appendix 5 continued

Substance	Formula	Heat of formation at 18°C and constant pressure, kcal/mole
Benzophenon (solid)	$C_{13}H_{10}O$	14,1
Potassium bicarbonate	$KHCO_3$	230,2
Sodium bicarbonate	$NaHCO_3$	226,4
Potassium bioxalate	KHC_2O_4	255,3
Sodium bioxalate (anhydrous)	$NaHC_2O_4$	257,7
Sodium bioxalate (hydrate)	$NaC_2O_5H_3$	330,1
Bisdiphenylcarbamide	$C_{26}H_{22}O_2N_4$	—6,51
Bitetryl	$C_{14}H_6O_{16}N_{10}$	—27,48
Ammonium bichromate	$(NH_4)_2 Cr_2O_7$	423,6
Potassium bichromate	$K_2Cr_2O_7$	483
Sodium bichromate	$Na_2Cr_2O_7$	471
Borneol	$C_{10}H_{18}O$	92,8
n. Butane (gas)	C_4H_{10}	31,6
n. Butane (liquid)	C_4H_{10}	36,7
Butadiene-1.3 (gas)	C_4H_6	—24,9
Butadiene-1.3 (liquid)	C_4H_6	—19,8
Butanediol-1.2	$C_4H_{10}O_2$	126,2
Butanediol-1.3	$C_4H_{10}O_2$	124,1
Butanediol-2.3	$C_4H_{10}O_2$	130,4
Butanol-1	$C_4H_{10}O$	81,5
Butanone	C_4H_8O	68,9
Butene-1 (gas)	C_4H_8	1,5
Butene-2 (cis)	C_4H_8	3,1
Butene-2 (trans)	C_4H_8	3,9
Isobutene (gas)	C_4H_8	5,1
Cotton hygroscopic*	—	q_v — 4120 cal/g
Vinylchloride (gas)	C_2H_3Cl	—9
Vinylchloride (liquid)	C_2H_3Cl	—4,1
Water (liquid)	H_2O	68,37
Water (gas)	H_2O	57,78

Appendix 5 continued

Substance	Formula	Heat of formation at 18°C and constant pressure, kcal/mole
Wax, Candelilla* (m-p. 64-66°C)	—	q_v = 10115 cal/g
Wax, lignite* (m-p. near 80°C)	—	q_v = 10660 .
Beeswax* (m-p. near 75°C)	—	q_v = 11050 .
Beeswax* (m-p. near 60°C)	—	q_v = 10250 .
n. Geksan (liquid)	C_6H_{14}	50,4
Hexanitrodiphenylamin	$C_{12}H_5O_{12}N_7$	—5,32
Methylentetramine (solid)	$C_6H_{12}N_4$	—27,9
Hexamethylenetriperoxidediamine	$C_6H_{12}N_2O_6$	84,8
Hexachlorethane (solid)	C_2Cl_6	53,9
n. Heptane (liquid)	C_7H_{16}	57,2
Hydrazinehydrate	$N_2H_4H_2O$	57,9
Hydrazine anhydrous (liquid)	N_2H_4	—12,3
Alumina	Al_2O_3	399
Glycerine	$C_3H_8O_3$	161,2
α-d-Glucose	$C_6H_{12}O_6$	307
α-d-Glucose hydrate	$C_6H_{14}O_7$	378,2
Mercury fulminate	$HgC_2O_2N_2$	—64,1
Silver fulminate	$AgCON$	—42,8
Diurethane of ethylenediamine ethyl (juinite)	$CH_2-NH-COO\ C_2H_5$ $\vert$ $CH_2-NH-COO\ C_2H_5$	236,9
Diammonium phosphate	$(NH_4)_2HPO_4$	372,8
Nitrogen peroxide (gaseous)	N_2O_4	—3,1
Nitrogen peroxide (liquid)	N_2O_4	—12,2
Chlorine dioxide (gas)	ClO_2	—23,5
Chlorine dioxide (liquid)	ClO_2	—17,0
Decahydronaphthalene (trans)	$C_{10}H_{18}$	60,1
Decahydronaphthalene (cis)	$C_{10}H_{18}$	58,0
Diazobenzolnitrate	$C_6H_5N_3O_3$	—42,3
Diamylphthalate	$C_{18}H_{26}O_4$	219,4
n-Diaminobenzene	$C_6H_8N_2$	+1,8
Dianthracene (solid)	$C_{28}H_{20}$	—61,2

Appendix 5 continued

Substance	Formula	Heat of formation at 18°C and constant pressure, kcal/mole
Cellulose diacetate	$C_{9.83}H_{13.83}O_{6.915}$	322,99
Diacetine	$C_7H_{12}O_5$	269,68
Dibutylphthalate	$C_{16}H_{22}O_4$	207,2
Diethyleneglycol	$C_4H_{10}O_3$	151,1
Dimethylapidate (liquid)	$C_8H_{14}O_4$	213,4
Dimethylamine (gas)	C_2H_7N	8,2
Dimethylamine (liquid)	C_2H_7N	14,7
Dimethyl aniline (liquid)	$C_8H_{11}N$	11,7
Dimethylhydrazine (symm.)	$C_2H_8N_2$	—11,5
Dimethylhydrazine (asymm.)	$C_2H_8N_2$	—10,7
4.4'-Dimethyldiphenylamine	$C_{14}H_{15}N$	6,50
Dimethyldiphenylcarbamide (symm.)	$C_{15}H_{16}ON_2$	21,5
Dimethylcarbamide (solid)	$C_3H_8O_3N_2$	173,4
Dimethylolnitropropane (Nitro-2 ethyl-2-propanediol-1.3)	$C_5H_{11}O_4N$	144,7
Dimethyloxalate (solid)	$C_4H_6O_4$	- 87,6
N-Dimethylformamide	C_3H_7ON	57,59
Dyne	$C_4H_8N_4O_8$	76,3
Dinitrate dioxyethyl-dinitrooxamide	$C_6H_8O_{12}N_6$	130,9
Dinitrate diethyleneglycol	$C_4H_8O_7N_2$	104,2
Dinitrate hexamethylene-diamine	$C_6H_{18}O_6N_4$	184,2
Dinitrate ethyleneglycol	$C_2H_4N_2O_6$	50,25
Dinitrate 2-methyl-2-nitro-propanediol-1.3	$C_4H_7O_8N_3$	91,3
Dinitrate ethylenediamine	$C_2H_{10}O_6N_4$	156,4
Dinitrate ethyl diurethane-ethylenedinitramine	$C_8H_{12}N_6O_{14}$	238,9
Dinitrate 2-ethyl-2-nitro-propanediol-1.3	$C_5H_9O_8N_3$	88,6
2.4-Dinitroaniline	$C_6H_3O_4N_3$	19,6
Dinitroaminophenol	$C_6H_5N_3O_5$	61,63
2.4-Dinitroanisole	$C_7H_6N_2O_5$	46,42
2.6-Dinitroanisole	$C_7H_6N_2O_5$	47,2
m-Dinitrobenzene	$C_6H_4N_2O_4$	8,6
2.4-Dinitrodimethyl aniline	$C_8H_9N_3O_4$	10,75

Appendix 5 continued

Substance	Formula	Heat of formation at 18°C and constnat pressure, kcal/mole
Dinitrobutyleneglycol-diurethane	$C_6H_{10}O_8N_4$	200,71
2.4-Dinitrodiphenylamine	$C_{12}H_9O_4N_3$	—2,59
2.4-Dinitrometaxylol	$C_8H_8N_2O_4$	22,8
4.6-Dinitrometaxylol	$C_8H_8N_2O_4$	26,7
1.6-Dinitro-N-methyl aniline	$C_7H_7O_4N_3$	6,55
2.4-Dinitronaphtol-1	$C_{10}H_6N_2O_5$	45,4
2.4-Dinitronaphtholate-1-sulfonate-7-dipotassium sextahydrate	$C_{10}H_7O_{9.5}N_2SK_2$	488,3
1.5-Dinitronapthalene	$C_{10}H_6O_4N_2$	—3,5
1.8-Dinitronapthalene	$C_{10}H_6O_4N_2$	—6,6
Dinitrosopentamethylene-tetramine	C_5H [illegible] O_2N_6	—52,0
2.6-Dinitrophenylmethyl-nitramine	$C_7H_6O_6N_4$	—6,10
2.4-Dinitrophenylmethyl-nitramine	$C_7H_6O_6N_4$	—0,7
4.6-Dinitroorthocresol	$C_7H_6N_2O_5$	69,78
2.6-Dinitroparacresol	$C_7H_6N_2O_5$	60,23
1.1-Dinitropropane (liquid)	$C_3H_6N_2O_4$	41,5
1.3-Dinitropropane (liquid)	$C_3H_6N_2O_4$	54,3
2.2-Dinitropropane (solid)	$C_3H_6N_2O_4$	45,6
2.4-Dinitroresorcine	$C_6H_4N_2O_6$	102,1
4.6-Dinitroresorcine	$C_6H_4N_2O_6$	107,9
2.4-Dinitrotoluene	$C_7H_6N_2O_4$	18,7
2.6-Dinitrotoluene	$C_7H_6N_2O_4$	4,7
2.4-Dinitrophenol	$C_6H_4N_2O_5$	56,4
2.6-Dinitrophenol	$C_6H_4N_2O_5$	51,9
2.4-Dinitrophenetol	$C_8H_8N_2O_5$	56,09
2.4-Dinitrophenoxyethylnitrate	$C_8H_7N_3O_8$	70,1
2.4-Dinitrophenylhydrazine	$C_6H_6O_4N_4$	—9,2
1.2-Dinitroethane (solid)	$C_2H_4N_2O_4$	43,0
Dinitroethyl benzene (liquid)[1]	$C_8H_8N_2O_4$	22,4

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[1] Mixture of isomers

Appendix 5 continued

Substance	Formula	Heat of formation at 18°C and constant pressure, kcal/mole
Dioxane	$C_4H_8O_2$	89,6
Dipentaerythritol	$C_{10}H_{22}O_7$	380,2
Dipentaerythritehexanitrate	$C_{10}H_{16}N_6O_{19}$	238,6
Dipicrilamine	$C_{12}H_5O_{12}N_7$	—5,32
Diphenyl (solid)	$C_{12}H_{11}N$	—28,2
Diphenyl	$C_{12}H_{10}$	—19,2
Diphenylmethane (liquid)	$C_{13}H_{12}$	—15,7
Diphenylcarbamide (asymm)	$C_{13}H_{12}ON_2$	32,6
Diphenylnitrosamine	$C_{12}H_{10}N_2O$	—48,9
Diphenylurethane ethyl (solid)	$C_{15}H_{15}NO_2$	73,9
Diphenylphthalate	$C_{20}H_{14}O_4$	122,07
Dichlormethane	CH_2Cl_2	30,8
1.1-Dichlorethane	$C_2H_4Cl_2$	40,6
1.2-Dichlorethane	$C_2H_4Cl_2$	40,5
Dicetyl (solid)	$C_{32}H_{66}$	247,2
Dicyandiamide	$C_2H_4N_4$	—4,5
Diethylamine (liquid)	$C_4H_{11}N$	27,2
Diethyldiphenylcarbamide (symm)	$C_{17}H_{20}ON_2$	31,9
Diethyleneglycol	$C_4H_{10}O_3$	151,1
Diethylphthalate	$C_{12}H_{14}O_4$	180,5
n. Dodecane (liquid)	$C_{12}H_{26}$	59,36
Wood of oak*	—	
trunk	—	$q_v = 4622$ cal/g
branch	—	$q_v = 4583$ "
Wood of alder*	—	
trunk	—	$q_v = 4715$ "
branch	—	$q_v = 4500$ "
Dulcite	$C_6H_{14}O_6$	324,5
Nitrous oxide (gas)	N_2O	—19,65
Isoamylphthalate	$C_{18}H_{26}O_4$	229,54
Isobutane (liquid)	C_4H_{10}	38,0

Appendix 5 continued

Substance	Formula	Heat of formation at 18°C and constant pressure, kcal/mole
Isobutene (gas)	C_4H_8	5,1
Isopropylnitrate	$C_3H_7O_3N$	54,62
Potassium ferrocyanide	$K_4Fe(CN)_6$	131,9
Potassium ferricyanide	$K_3Fe(CN)_6$	48,5
Potassium acetate	$KC_2H_3O_2$	174,7
Camphor, natural (solid)	$C_{10}H_{16}O$	76,9
Carbazole	$C_{12}H_9N$	—26,84
Aluminum carbide	Al_4C_3	50
Iron carbide	Fe_2C	—5,8
Calcium carbide	CaC_2	14,5
Barium carbonate	$BaCO_3$	290,9
Potassium carbonate	K_2CO_3	274,46
Calcium carbonate (calcite)	$CaCO_3$	289,5
Magnesium carbonate	$MgCO_3$	265,5
Sodium carbonate	Na_2CO_3	269,89
Lead carbonate	$PbCO_3$	167,8
Strontium carbonate	$SrCO_3$	291,7
Castor oil*	—	$q_v = 9620$ cal/g
Natural rubber*	—	$q_v = 10700$
Cinnabar	HgS	14
Nitric acid (liquid)	HNO_3	41,66
Nitric acid (gas)	HNO_3	34,4
Nitric acid hydrazoic (liquid)[1]	HN_3	—64,37
Nitric acid hydrazoic (gas)[1]	HN_3	—71,66
Nitric acid benzoic	$C_7H_6O_2$	94,1
Nitric acid tartaric (right, solid)	$C_4H_6O_6$	307,7

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[1] At 25°C.

Appendix 5 continued

Substance	Formula	Heat of formation at 18°C and constant pressure, kcal/mole
Formic acid	CH_2O_2	100,0
Naphtol-1-dinitro-2.4-sulfone-7 (dihydrate) acid	$C_{10}H_{10}O_{10}N_2S$	314,6
Oleic acid	$C_{18}H_{34}O_2$	149,2
Picramic acid	$C_6H_5N_3O_5$	61,63
Picric acid	$C_6H_3N_3O_7$	54,4
Salicylic acid (solid)	$C_7H_6O_3$	146,2
Sulfuric acid (liquid)	H_2SO_4	193,75
Sulfuric acid (hydrate, liquid)	$H_2SO_4 \cdot H_2O$	268,74
Sulfuric acid, (dilute ∞H_2O)	H_2SO_4	215,8
Prussic acid	HCN	—30,7
Stearic acid	$C_{18}H_{36}O_2$	223,8
Styphnic acid	$C_6H_3N_3O_8$	106,66
Trinitrobenzoic acid	$C_7H_3O_8N_3$	101,0
Acetic acid (liquid)	$C_2H_4O_2$	117,7
Phosphoric acid (solid)	H_3PO_4	303,37
Phthalic acid (solid)	$C_8H_6O_4$	191,0
Hydrofluoric acid (gaseous)	HF	64,2
Hydrofluoric acid (dilute)	HF	78,75
Furan-3-carbonic acid (solid)	$C_5H_4O_3$	121,5
Hydrochloric acid (gaseous)	HCl	21,9
Acid hydrochloric acid (dilute)	HCl	39,6
Chloric acid (dilute, hydrate)	$HClO_4$	31,7
Oxalic acid (anhydrous, solid)	$H_2C_2O_4$	197,3
Oxalic acid (hydrate, solid)	$H_2C_2O_4 2H_2O$	341,5
Cellulose	$C_6H_{10}O_5$	230,3
Coke from nut shells*	—	q_v = 4637 cal/g

Appendix 5 continued

Substance	Formula	Heat of formation at 18°C and constant pressure, kcal/mole
Starch	$C_6H_{10}O_5$	230,8
m-Cresol	C_7H_8O	48,3
Cryolite, potassium	K_3AlF_6	[illegible]7,57
Cryolite, sodium	Na_3AlF_6	748,5
Xylan* (from oat straw)	—	$q_v = 3952$ cal/g
Xylols		
orthoxylene (liquid)	C_8H_{10}	10,4
metaxylol (liquid)	C_8H_{10}	10,9
paraxylene (liquid)	C_8H_{10}	10,5
d-Xylose	$C_5H_{10}O_5$	253,4
Cupren	$\frac{1}{n}(C_2H_2)_n$	−8,6
Lignin (from wood of fir)*	—	$q_v = 6277$ cal/g
Lignol (from oat straw)*	—	$q_v = 6076$ cal/g
β-Lactose	$C_{12}H_{22}O_{11}$	534,8
Mannitehexanitrate	$C_6H_8N_6O_{18}$	162,6
Mannite	$C_6H_{14}O_6$	322,3
Melamine	$C_3H_6N_6$	17,98
Methane (gas)	CH_4	18,3
Methylamine (gas)	CH_5N	7,3
Methylhydrazine	CH_6N_2	−12,4
α-Methylglucoside	$C_7H_{14}O_6$	296,6
N-Methyldiphenylamine	$C_{13}H_{13}N$	−25,42
4-Methyldiphenylamine	$C_{13}H_{13}N$	−8,27
N-Methyl-N'N'-diphenylcarbamine	$C_{14}H_{14}ON_2$	29,1
N-Methyl-2.4-dinitroaniline	$C_7H_7N_3O_4$	19,4
Methylcarbamide	$C_2H_4ON_2$	78,60

Appendix 5 continued

Substance	Formula	Heat of formation at 18°C and constant pressure, kcal/mole
Methylisolentylketone	$C_6H_{12}O$	94,26
Methylnitrate (liquid)	CH_3NO_3	37
β-Methylnapthalene	$C_{11}H_{10}$	—2,5
Methyltetraline (liquid)	$C_{11}H_{14}$	19,6
N-Methylphenyl-N'-methylcarbamide	$C_9H_{12}ON_2$	54,01
N-Methylphenyl-N'-ethylcarbamide	$C_{10}H_{14}ON_2$	75,16
Ethyl methylphenylurethane (liquid)	$C_{10}H_{13}NO_2$	96,6
N-Methyl-N'-ethyl-NN'diphenylcarbamide	$C_{16}H_{18}ON_2$	30,1
Methylquinoline	$C_{10}H_9N$	—36,1
Methylenechloride (liquid)	CH_2Cl_2	30,8
Methylchloride (gas)	CH_3Cl	20,1
Methylcyclohexane (liquid)	C_7H_{14}	49,7
Monoacetin	$C_5H_{10}O_4$	218,52
Carbamide	CH_4N_2O	79,6
Wood meal*	—	$q_v = 4690$ cal/g
Cork meal*	—	$q_v = 6570$
Hydrogen arsenide	AsH_3	—43,6
Oat chaff*	—	$q_v = 5052$ cal/g
Sodium acetate	$C_2H_3O_2Na$	171,3
Napthalene	$C_{10}H_8$	—15,0
N-α-naphthyl)-N'-diphenylcarbamide	$C_{23}H_{18}ON_2$	—12,65
α-Naphtol	$C_{10}H_8O$	30,8
β-Naphtol	$C_{10}H_8O$	32,9
OS Naphtol yellow	$C_{10}H_{10}O_{10}N_2S$	314,6
β-Naphtylamine (solid)	$C_{10}H_9N$	—8,2
Neno (dioxyethyldinitroxamide)	$C_6H_8O_{12}N_6$	130,9
Neopentane (tetramethylmethane) (liquid)	C_5H_{12}	47,2

Appendix 5 continued

Formula	Substance	Heat of formation at 18°C and constant pressure, kcal/mole
Ammonium nitrate	NH_4NO_3	87,36
Aniline nitrate (solid)	$C_6H_8N_2O_3$	52,7
Barium nitrate	$Ba(NO_3)_2$	236,9
Hydrazine nitrate	$N_2H_5NO_3$	59,8
Hydroxyethylmethylnitramine nitrate	$C_3H_7O_5N_3$	45,8
Guanidine nitrate	$CH_6N_4O_3$	91,2
Dimethylamine nitrate	$C_2H_8O_3N_2$	80,0
2.4-dinitrophenoxyethanol nitrate	$C_8H_7O_8N_3$	67,44
Diethylamine nitrate	$C_4H_{12}O_3N_2$	101,2
Potassium nitrate	KNO_3	118,09
Calcium nitrate	$Ca(NO_3)_2$	224,04
Methylamine nitrate	$CH_6O_3N_2$	84,8
Carbamide nitrate	$CN_3O_4H_5$	134,84
Sodium nitrate	$NaNO_3$	111,72
bis-ammonium nitrate (bis-nitroxyethylammonium nitrate)	$(CH_2ONO_2—CH_2)_2NH\cdot HNO_3$	137,6
Nitroxyethylammonium nitrate	$C_2H_7N_3O_6$	112,8
Silver nitrate	$AgNO_3$	28,9
Lead nitrate	$Pb(NO_3)_2$	106,89
Strontium nitrate	$Sr(NO_3)_2$	233,2
Tetramethylammonium nitrate	$C_4H_{12}O_3N_2$	80,8
Trimethylamine nitrate	$C_3H_{10}O_3N_2$	74,6
2, 4, 6-trinitrophenylglycol nitrate	$C_8H_6O_{10}N_4$	72,55
Triethylamine nitrate	$C_6H_{16}O_3N_2$	100,4
Ethanolamine nitrate	$C_2H_8O_4N_2$	138,9
Ethylamine nitrate	$C_2H_8O_3N_2$	88,0
Ethylolamine nitrate	$CH_2OHCH_2NH_2HNO_3$	138,9
Aluminum nitride (crystalline)	AlN	80
Magnesium nitride	Mg_3N_2	110,5
Silver nitride	Ag_3N	—61
Ammonium nitrite	NH_4NO_2	61,5
Sodium nitrite	$NaNO_3$	88,2
Nitroanilines orthonitroaniline	$C_6H_6O_2N_2$	9,60

Appendix 5 continued

Substance	Formula		Heat of formation at 18°C and constant pressure, kcal/mole
Nitroanilines			
methanitroaniline	$C_6H_6O_2N_2$		10,10
paranitroaniline	$C_6H_6O_2N_2$		12,0
N-Nitro-N'-aminoguanidine	$CH_6N_5O_2$		−1,2
Nitrobenzene (liquid)	$C_6H_5NO_2$		3,2
1-Nitrobutane (liquid)	$C_4H_9NO_2$		47,5
2-Nitrobutane (liquid)	$C_4H_9NO_2$		51,6
3-Nitrobutanol-2 (liquid)	$C_4H_{10}O_3N$		129
Nitrodicyandiamidine	$C_2H_5O_3N_5$		75,73
Nitroglycerine	$C_3H_5N_3O_9$		88,63
Nitroguanidine	$CH_4N_4O_2$		21,86
Nitroguanylcarbamide	$C_2H_5N_5O_3$		75,8
o-Nitrodiphenylamine	$C_{12}H_{10}O_2N_2$		12,65
Nitroisobutantriol (solid)	$C_4H_9O_5N$		178,3
p-Nitrosodiphenylamine	$C_{12}H_{10}N_2O$		−15,4
Nitrocellulose 11,50% N	—	Heats of formation at constant volume in cal/g	692,3
. 11,60% N	—		686,2
. 11,70% N	—		680,1
. 11,80% N	—		674,0
. 11,90% N	—		668,0
. 12,00% N	—		661,9
. 12,10% N	—		655,8
. 12,20% N	—		649,7
. 12,30% N	—		643,7
. 12,40% N	—		637,6
. 12,50% N	—		631,5
. 12,60% N	—		625,4
. 12,70% N	—		619,4
. 12,80% N	—		613,3
. 12,90% N	—		607,2
. 13,00% N	—		601,1
. 13,10% N	—		595,0
. 13,20% N	—		589,0
. 13,30% N	—		582,9
. 13,40% N	—		576,8
. 13,50% N	—		570,7

Appendix 5 continued

Substance	Formula	Heat of formation at 18°C and constant pressure, kcal/mole
Nitrosodiphenylamine	$C_{12}H_{10}N_2O$	—50,9
Nitromethane (liquid)	CH_3NO_2	21,86
2-Nitro-2-methyl propanol-1 (solid)	$C_4H_9O_3N$	99,8
2-Nitro-2-methyl-propanediol-1.3 (solid)	$C_4H_9O_4N$	138,3
Nitrometriol	$C_5H_9N_3O_9$	107,88
Nitrocarbamide	$CH_3O_3N_3$	67,65
1-Nitronaphthalene	$C_{10}H_7O_2N$	—7,3
5-Nitroorthotoluidine	$C_7H_8O_2N_2$	24,6
3-Nitroparatoluidine	$C_7H_8O_2N_2$	20,0
Nitropentaglycerine	$C_3H_9N_3O_9$	107,88
1-Nitropropane (liquid)	$C_3H_7NO_2$	41,5
2-Nitropropane (liquid)	$C_3H_7NO_2$	45,3
m-Nitrotoluene	$C_7H_7NO_2$	10,7
Nitrotoluidines		
5-Nitroorthotoluidine	$C_7H_8O_2N_2$	24,6
3-Nitroparatoluidine	$C_7H_8O_2N_2$	20,0
Nitrophenetoles		
orthonitrophenetole (liquid)	$C_8H_9NO_3$	41,7
metanitrophenstole (solid)	$C_8H_9NO_3$	53,7
paranitrophenetol	$C_8H_9NO_3$	56,9
Nitrophenols		
orthonitrophenol	$C_6H_5NO_3$	50,5
metanitrophenol	$C_6H_5NO_3$	53,2
paranitrophenol	$C_6H_5NO_3$	49,6
Nitroethane (liquid)	$C_2H_5NO_2$	34,4
2-Nitroethanol	$C_2H_5NO_3$	84,5
2-Nitro-2-ethyl-propandiol-1.3	$C_5H_{11}O_4N$	144,7
o-Nitroethyl benzene (liquid)	$C_8H_9O_2N$	15,25
n-Nitroethyl benzene (liquid)	$C_8H_9O_2N$	16,90
n-Nonane	C_9H_{20}	60,8
Oat straw*	—	q_v = 4208 cal/g

Appendix 5 continued

Substance	Formula	Heat of formation at 18°C and constant pressure, kcal/mole
Ozone (gas)	O_3	—34,5
Ozonide potassium	KO_3	62
Oxide nitrogen (gas)	NO	—21,6
Oxide aluminum (crystalline)	Al_2O_3	399
Oxide beryllium (solid)	BeO	147,3
Oxide tungsten	WO_3	200,2
Oxide diphenyl	$C_{12}H_{10}O$	13,2
Oxide ferrous	Fe_2O_3	196,5
Oxide ferric	Fe_3O_4	266,9
Oxide calcium	CaO	151,9
Oxide silicon (quartz) (solid)	SiO_2	208
Oxide silicon (vitreous) (solid)	SiO_2	205
Oxide magnesium	MgO	143,9
Oxide copper	CuO	38,5
Oxide propylene (liquid)	C_3H_6O	35,2
Oxide lead (red)	PbO	52,46
Oxide antimony (octahedral)	Sb_2O_3	166,6
Oxide carbon (gas)	CO	26,88
Oxide chromium (green)	Cr_2O_3	268
Oxide zinc (alloy)	ZnO	83,4
Oxide zirconium (monoclinic)	ZrO_2	258,2
Oxide ethylene (liquid)	C_2H_4O	23,3
Octonitrate saccharose	$C_{12}H_{14}O_{27}N_8$	331,5
Olive oil*	—	$q_v = 9400$ cal/g
Oxalate of ammonium anhydrous	$C_2O_4H_8N_2$	267,2
Oxalate ammonium hydrate	$C_2O_5H_{10}N_2$	341,5
Oxalate barium	BaC_2O_4	327,6
Oxalate potassium	$K_2C_2O_4$	320,8

Appendix 5 continued

Substance	Formula	Heat of formation at 18°C and constant pressure, kcal/mole
Oxalate potassium hydrate	$K_2C_2H_2O_5$	392,1
Oxalate calcium	CaC_2O_4	325,2
Oxalate sodium	$Na_2C_2O_4$	314,7
Oxalate strontium	SrC_2O_4	327,7
8-Hydroxyquinoline	C_9H_7NO	24,6
n. Octadecane (solid)	$C_{18}H_{38}$	144,5
Paraffin*		
solid (m-p. 52.5-53°)	—	$q_v = 11\,190$ cal/g
liquid	—	$q_v = 10\,965$
Paraphenylenediamine	$C_6H_8N_2$	1,8
n. Pentane (liquid)	C_5H_{12}	44,0
Pentaglycerine	$C_5H_{12}O_3$	180,2
Pentamethylenedinitrosotetramine	$C_5H_{10}N_6O_2$	—52,5
Pentanitrate anhydroenneaheptite	$C_9H_{13}O_{16}N_5$	194,0
Pentachloroethane (liquid)	C_2HCl_5	49,2
Pentaerythritol	$C_5H_{12}O_4$	222,3
Peroxide barium	BaO_2	149
Peroxide hydrogen (liquid)	H_2O_2	44,1
Peroxide manganese	MnO_2	123
Peroxide potassium	K_2O_2	117
Peroxide sodium (solid)	Na_2O_2	124,04
Peroxide lead	PbO_2	65,0
Peroxide ethyl	$C_4H_{10}O_2$	102,8

Appendix 5 continued

Substance	Formula	Heat of formation at 18°C and constant pressure, kcal/mole
Permanganate potassium	$KMnO_4$	192,9
Permanganate calcium	$Ca(MnO_4)_2$	362
Permanganate sodium	$NaMnO_4$	181
Pernitride carbon (solid)	CN_4	—[illegible],6
Perchlorate ammonium	NH_4ClO_4	70,2
Perchlorate barium	$Ba(ClO_4)_2$	1[illegible]4,3
Perchlorate hydrazine	$N_2H_5ClO_4$	42,0
Perchlorate potassium	$KClO_4$	104,5
Perchlorate lithium[1]	$LiClO_4$	91,70
Perchlorate sodium	$NaClO_4$	93
Perchlorethylene	C_2Cl_4	16,4
Picrate ammonium (red or yellow)	$C_6H_6O_7N_4$	9[illegible]
Picrate potassium	$KC_6H_2N_3O_7$	116,5
Picrate sodium	$NaC_6H_2N_3O_7$	111,5
Peperidine	$C_5H_{11}N$	20,6
N-Piperidine-N'-diphenylcarbamide	$C_{18}H_{20}ON_2$	30,75
Picrichloride	$C_6H_2O_6N_3Cl$	—7,0
Pyridine	C_5H_5N	—22,5
Polyrinylacetate	—	$q_v = 5620$ cal/g
Polyisobutylene (solid)	$\frac{1}{n}(C_4H_8)_n$	23,0
Polyoxymethylene	$\frac{1}{n}(CH_2O)_n$	42,5
Polystyrene	$\frac{1}{n}(C_6H_5C_2H_3)_n$	—4,4
Polyethylene (solid)	$\frac{1}{700}(C_2H_4)_{700}$	14,0
Cork*	—	$q_v = 6570$ cal/g
Propane (gas)	C_3H_8	26,1
Propane (liquid)	C_3H_8	29,9
Propanediol-1.2	$C_3H_8O_2$	120,4

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[1] At 25°C.

Appendix 5 continued

Substance	Formula	Heat of formation at 18°C and constant pressure, kcal/mole
Propanediol-1.3	$C_3H_8O_2$	124,9
n.Propylchloride (liquid)	C_3H_7Cl	39,8
n.Propyl benzene (liquid)	C_9H_{12}	13,8
Propylene (gas)	C_3H_6	—3,4
Ramie*	—	$q_v = 4190$ cal/g
Soot*		
dried at 100°C	—	$q_v = 7810$ "
degassed at 1000°C	—	$q_v = 8270$ "
Saccharose	$C_{12}H_{22}O_{11}$	536,5
Hydrogen sulfide (gas)	H_2S	4,8
Carbon bisulfide (liquid)	CS_2	—29,4
Carbon bisulfide (gas)	CS_2	—22
Silicide calcium	$CaSi_2$	161,8
"	Ca_2Si_2	170,6
Straw of grasses*	—	$q_v = 4214$ cal/g
Alcohol amyl (n.)	$C_5H_{12}O$	85,7
Alcohol butyl (n.)	$C_4H_{10}O$	81,5
Alcohol hexyl (n.)	$C_6H_{14}O$	91,9
Alcohol heptyl (n.)	$C_7H_{16}O$	97,8
Alcohol isopropyl	C_3H_8O	77,8
Alcohol methyl	CH_4O	57,5
Alcohol octyl (n.)	$C_8H_{18}O$	103,9
Alcohol propyl (n.)	C_3H_8O	74,6
Alcohol tetrahydrofurfuryl	$C_5H_{10}O_2$	104,9
Alcohol furyl (2-furylcarbinol)	$C_5H_6O_2$	98,5
Alcohol ethyl	C_2H_6O	67,1
Stearate calcium	$CaC_{36}H_{70}O_4$	802,6
Styrene (liquid)	C_8H_8	—20,8

Appendix 5 continued

Substance	Formula	Heat of formation at 18°C and constant pressure, kcal/mole
Styphnate lead (hydrate)	$C_6H_3N_3O_9Pb$	204,1
Succinamide	$C_4H_8O_2N_2$	139,98
Sulfate ammonium	$(NH_4)_2SO_4$	281.46
Sulfate barium	$BaSO_4$	340,4
Sulfate calcium-ammonium	$Ca(NH_4)_2(SO_4)_2H_2O$	694,5
Sulfate potassium	K_2SO_4	342,66
Sulfate calcium	$CaSO_4$	340,7
Sulfate lead	$PbSO_4$	219,5
Sulfate strontium	$SrSO_4$	345,3
Sulfate sodium	Na_2SO_4	330,48
Sulfide nitrogen (solid)	NS	−31,9
Sulfide barium	BaS	111,2
Sulfide ferrous	FeS	23,1
Sulfide ferric (pyrite)	FeS_2	42,5
Sulfide iron (marcassite)	FeS_2	38,9
Sulfide potassium	K_2S	121,5
Sulfide calcium	CaS	113.4
Sulfide magnesium	MgS	82,2
Sulfide arsenic (solid, realgar)	As_2S_2	30
Sulfide sodium	Na_2S	89,8
Sulfide mercury* (cinnabar)	HgS	14
Sulfide silver	Ag_2S	7
Sulfide strontium	SrS	113.1
Sulfide antimony (black)	Sb_2S_3	36,8
Sulfide zinc	ZnS	44
Sulfide phosphorus (solid)	P_4S_3	77,5
Sulfide lead	PbS	22,38
Tartramide	$C_4H_8O_4N_2$	296,36
Turpentine*	—	$q_v = 10700$ cal/g
Tetrahydrocarbasolcarbamide	$C_{13}H_{14}ON_2$	221,86
1,2,3,4-Tetrahydronapthalene (liquid)	$C_{10}H_{12}$	10,5

Appendix 5 continued

Substance	Formula	Heat of formation at 18°C and constant pressure, kcal/mole
Tetrahydroquinoline	$C_9H_{11}N$	−2,9
Tetramethylomethane	$C_5H_{12}O_4$	221,2
Tetraline	$C_{10}H_{12}$	19,5
Tetranitrate α-methyl-d-glucoside	$C_7H_{10}O_{14}N_4$	200,6
2,3,4,6-Tetranitroaniline	$C_6H_3O_8N_5$	−17,1
Tetranitrocarbazole	$C_{12}H_5O_8N_5$	−1,69
Tetranitromethane (liquid)	$C(NO_2)_4$	−8,4
1,3,6,8-Tetranitronapthalene	$C_{10}H_4O_8N_4$	−1,6
Tetranitrosulfoxydiphenylamine	$C_{12}H_5O_9N_5S$	114,95
Tetrachloroethane (symm.) (liquid)	$C_2H_2Cl_4$	50,7
Tetrachlorethylene (liquid)	C_2Cl_4	16,4
Tetraethylcarbamide	$C_9H_{20}ON_2$	134,22
Tetryl	$C_7H_5N_5O_8$	−4,70
Thiodiphenylamine	$C_{12}H_9NS$	−12,42
Thiocarbamide	CH_4N_2S	18,7
Thiophene (liquid)	C_4H_4S	−19,5
Toluene (liquid)	C_7H_8	+1,0
Toluidines[1]	C_7H_9N	+4,8
Peat*	—	$\varphi_0 = 5100$ cal/g
Triacetate cellulose	$C_{11,786}H_{15,786}O_{7,893}$	373,40
Triacetin	$C_9H_{14}O_6$	320,27
Tribenzilamine	$C_{21}H_{21}N$	−29,09
Trimethylamine	C_3H_9N	9,3
1,3,5-Trimethylbenzol (liquid)	C_9H_{12}	19,8
Trimethyleneglycol	$C_3H_8O_2$	124,9
Trimethylcarbamide	$C_4H_{10}ON_2$	79,75
Trymethylolmethylmethane (solid)	$C_5H_{12}O_3$	180,2
Trimethylolethylmethane (solid)	$C_6H_{14}O_3$	181,0
Trimethylolnitromethane	$C_4H_9O_5N$	178,3
Diethylolamine trinitrate	$C_4H_{10}O_9N_4$	138,6

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[1] Approximate average data; applicable to all three isomers.

Appendix 5 continued

Substance	Formula	Heat of formation at 18°C and constant pressure, kcal/mole
Trinitrate nitroisobutylglycerine	$C_4H_6N_4O_{11}$	86,03
Trinitrate trimethylolethylmethane	$C_6H_{11}O_9N_3$	115,8
Trinitrate trimethylolmethylmethane	$C_5H_9N_3O_9$	107,88
Trinitroaniline	$C_6H_4N_4O_6$	20,07
2,4,6-Trinitroanisole	$C_7H_5N_3O_7$	20,79
2,4,6-Trinitro-1,3,5-tris(methylnitramino) benzene	$C_9H_9O_{12}N_9$	—26,8
1,3,5-Trinitrobenzene	$C_6H_3N_3O_6$	11,40
2,4,6-Trinitrocresol	$C_7H_5N_3O_7$	62,81
1,3,5-Trinitromesitylene	$C_9H_9N_3O_6$	33,7
2,4,6-Trinitrometaxylol	$C_8H_7N_3O_6$	26,2
2,4,6-Trinitrometacresol	$C_7H_5N_3O_7$	62,81
Trinitromethane	$CH(NO_2)_3$	19,1
1,3,8-Trinitronaphthalene	$C_{10}H_5O_6N_3$	—2,9
1,4,5-Trinitronaphthalene	$C_{10}H_5O_6N_3$	—5,8
2,4,6-Trinitroresorcine	$C_6H_3N_3O_8$	106,06
2,4,6-Trinitrotoluene	$C_7H_5N_3O_6$	17,5
Trinitropentaglycerine	$C_5H_9N_3O_9$	107,88
2,4,6-Trinitrophenol	$C_6H_3N_3O_7$	54,4
2,4,6-Trinitrophenetole	$C_8H_7N_3O_7$	51,08
bis-Trinitrophenylethylenedinitramine	$C_{14}H_8O_{16}N_{10}$	—27,48
2,4,6-Trinitrophenylhydrazine	$C_6H_5O_6N_5$	—5,8
2,4,6-Trinitrophenoxyethylnitrate	$C_8H_6N_4O_{10}$	70,0
2,4,6-Trinitrochlorbenzene	$C_6H_2O_6N_3Cl$	—7,0
1,3,5-Trinitroethylbenzene	$C_8H_7N_3O_6$	20,0
2,4,6-Trinitroethylbenzene	$C_8H_7N_3O_6$	21,4
Trinitrophenylethylnitramine	$C_8H_7N_5O_8$	7,70
a-Trioxymethylene	$\frac{1}{3}(CH_2O)_3$	41,9
Triphenylamine (solid)	$C_{18}H_{15}N$	—57,8
Trichlormethane	$CHCl_3$	34,8
Trichloroethylene	C_2HCl_3	12,4

Appendix 5 continued

Substance	Formula	Heat of formation at 18°C and constant pressure, kcal/mole
Triethylamine (liquid)	$C_6H_{15}N$	37,1
Triethyleneglycol	$C_6H_{14}O_4$	193,7
PETN	$C_5H_8N_4O_{12}$	129,37
Carbon dioxide (gas)	CO_2	94,51
Carbon amorphous*	—	$q_v = 8130$ cal/g
Phenanthrene (solid)	$C_{14}H_{10}$	—21,3
Phenetole	$C_8H_{10}O$	40,2
Phenol	C_6H_6O	40,9
Phenylbetanaphthylamine	$C_{16}H_{13}N$	—31,1
Phenylbetanaphthylnitrosoamine	$C_{16}H_{12}N_2O$	—69,7
Phosphide hydrogen (gas)	PH_3	2,3
Furfurole	$C_5H_4O_2$	49,0
Quinoline	C_9H_7N	—34,4
Quinaldine	$C_{10}H_9N$	—36,1
Chlorate barium	$Ba(ClO_3)_2$	176,6
Chlorate potassium	$KClO_3$	93,2
Chlorate calcium	$Ca(ClO_3)_2$	167
Chlorate sodium	$NaClO_3$	83,60
Chlorate strontium	$Sr(ClO_3)_2$	171
Chlorohydrin glycol	C_2H_5OCl	75
Chloride aluminum	$AlCl_3$	166,8
Chloride ammonium	NH_4Cl	74,95
Chloride barium	$BaCl_2$	205,28
Chloride potassium	KCl	104,36
Chloride calcium (alloyed)	$CaCl_2$	190,6
Chloride magnesium	$MgCl_2$	153,2
Chloride magnesium (hydrate)	$MgCl_2 \cdot H_2O$	231,9
Sodium chloride	$NaCl$	98,33
Chloride lead	$PbCl_2$	85,71
Chloride strontium	$SrCl_2$	197,87
Chloride zinc	$ZnCl_2$	99,55
Chloride nitrogen (solution in CCl_4)	NCl_3	—55,0

Appendix 5 continued

Substance	Formula	Heat of formation at 18°C and constant pressure, kcal/mole
Chloroform (liquid)	$CHCl_3$	34,8
Chlorethylenes:		
gas	C_2H_3Cl	—9
liquid	C_2H_3Cl	—4,1
Chromate ammonium	$(NH_4)_2CrO_4$	276,9
Chromate potassium	K_2CrO_4	319,8
Chromate sodium	Na_2CrO_4	308
Cotton*	—	q_v = 4160 cal/g
Centralite I	$C_{17}H_{20}N_2O$	31,9
Centralite II	$C_{15}H_{16}ON_2$	21,5
Centralite III	$C_{16}H_{18}ON_2$	30,1
Cyanogen (gas)	C_2N_2	—72,9
Cyanamide	CH_2N_2	—13,7
Cyanide potassium	KCN	28,5
Cyanide calcium	CaC_2N_2	44,9
Cyanide sodium	$NaCN$	22,9
Cyanide mercury	HgC_2N_2	—61,8
Cyanurtriazide	C_3N_{12}	—219
Cyclohexane (liquid)	C_6H_{12}	41,0
Cyclohexanol (liquid)	$C_6H_{12}O$	86,5
Cyclohexylphthalate	$C_{20}H_{26}O_4$	227,80
Cycloheptane (liquid)	C_7H_{14}	40,5
Cyclopentane (liquid)	C_5H_{10}	27,9
Cyclopentanol (liquid)	$C_5H_{10}O$	74,3
Cyclotrimethylenetrinitramine	$C_3H_6N_6O_6$	—15,64
Cyclotrimethylenetrinitrosamine	$C_3H_6N_6O_3$	—66,79
Tetrachloride, carbon (liquid)	CCl_4	33,0
Silk, artificial*	—	q_v = 4400 ÷ 4440 cal/g
Wool, dry*	—	q_v = 5000

Appendix 5 continued

Substance	Formula	Heat of formation at 18°C and constant pressure, kcal/mole
Erythrite	$C_4H_{10}O_4$	219,4
Ethane (gas)	C_2H_6	21,1
Ethylamine (gas)	C_2H_7N	13,0
Ethylamine (liquid)	C_2H_7N	19,6
Ethyl, benzene (liquid)	C_8H_{10}	7,9
Ethylhydrogen peroxide	$C_2H_6O_2$	58,7
N-ethyl-N'N'-diphenyrbamide	$C_{15}H_{16}ON_2$	40,5
Ethylene	C_2H_4	—11,6
Ethylenebisdiphenylcarbamide	$C_{28}H_{26}O_2N_4$	54,01
Ethylene glycol	$C_2H_6O_2$	108,7
Ethylenedinitramine — ammonium	$C_2H_{12}N_6O_4$	81,0
Ethylnitramine	$C_2H_6N_2O_2$	21,3
Ethylnitrate (liquid)	$C_2H_5NO_3$	46
Ethylenchloride (liquid)	$C_2H_4Cl_2$	40,6
Ethylenedichloride (liquid)	$C_2H_4Cl_2$	40,5
Ethyltetryl	$C_8H_7N_5O_8$	7,70
Ethylphanylurethane, ethyl (liquid)	$C_{11}H_{15}NO_2$	105,7
Ethylchloride (liquid)	C_2H_5Cl	31,6
Ether, dimethyl (liquid)	C_2H_6O	49,6
Ether, diethyl (liquid)	$C_4H_{10}O$	67,6
Ether dimethyl sebacate (liquid)	$C_{12}H_{22}O_4$	247,6
Ether, dimethyl succinate (liquid)	$C_6H_{10}O_4$	200,8
Ether, methyl formate	$C_2H_4O_2$	92,4
Ether, ethyl formate	$C_3H_6O_2$	96,6
Ether, butyl acetate	$C_6H_{12}O_2$	129,4
Ether, isomayl acetate	$C_7H_{14}O_2$	138,3
Ether, isobutyl acetate	$C_6H_{12}O_2$	131,4
Ether, isopropyl acetate	$C_5H_{10}O_2$	125,3
Ether, methyl acetate	$C_3H_6O_2$	90,3
Ether, propyl acetate	$C_5H_{10}O_2$	122,6
Ether, ethyl acetate	$C_4H_8O_2$	114,6

Note: For a number of substances of natural or artificial origin, the composition of which is not strictly determined, instead of the heats of formation, are given the heats of combustion at constant volume in cal/g. In the table, these compounds are marked by an asterisk.

APPENDIX 6

HEATS OF COMBUSTION OF NITRO-COMPOUNDS TO CO_2, H_2O(liquid), N_2 AT CONSTANT VOLUME AND 25°C*

Substance	Formula	Heat of combustion, kcal/mole
Tetranitromethane	$C(NO_2)_4$	102,9
Trinitromethane	$CH(NO_2)_3$	124,5
Nitromethane	CH_3NO_2	169,4
Nitroethane	$C_2H_5NO_2$	322,2
Methylnitroacetate	$C_3H_5O_2NO_2$	343,18
Etilendinitramin, EDNA	$(CH_2NHNO_2)_2$	370,9
N-Nitroethylamine	$C_2H_5NHNO_2$	372,5
N-Nitrosuccinimide	$(CH_2CO)_2NNO_2$	436,9
1,1-Dinitropropane	$C_3H_6(NO_2)_2$	446,3
2,2-Dinitropropane	$C_3H_6(NO_2)_2$	442,2
1,3-Dinitropropane	$C_3H_6(NO_2)_2$	433,6
Hexogene	$(CH_2NNO_2)_3$	503,4
Trimethylolnitromethane	$(CH_2OH)_3CNO_2$	500,32
2-Nitropropane	$C_3H_7NO_2$	477,4
Bis-(trinitroethyl) nitramine	$[(NO_2)_3CCH_2]_2NNO_2$	486,0
N-(1,1-dinitroethyl)-1-nitroacetaldoxym	$CH_3CNO_2{:}NOC(NO_2)_2CH_3$	544,8
2-Nitro-2-methylpropanediol-1,3	$C_4H_9O_2NO_2$	545

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*From the summary table of Young, Case, et al., in Industrial and Engineering Chemistry, 8, 1376 (1956).

Appendix 6 continued

Substance	Formula	Heat of combustion, kcal/mole
2,2,3,3-Tetranitrobutane	$C_4H_6(NO_2)_4$	586,1
2-Nitro-2-Methylpropanol-1	$C_4H_9ONO_2$	585,59
3-Nitrobutanol-2	$C_4H_9ONO_2$	590,36
Bistrinitroethylcarbamide	$CO[NHC_2H_2(NO_2)_3]_2$	602,5
1-Nitrobutane	$C_4H_9NO_2$	637,6
2-Nitrobutane	$C_4H_9NO_2$	634,0
2,4,6-Trinitrophenol	$C_6H_2OH(NO_2)_3$	621,1
2,4,6-Trinitrochlorobenzene	$C_6H_2Cl(NO_2)_3$	643,202
2,4-Dinitrophenol	$C_6H_3OH(NO_2)_2$	648
Trinitroethyltrinitrobutyrate	$C_6H_6(NO_2)_6O_2$	661,0
2-Nitro-2-ethylpropanedoil-1,3	$C_5H_{11}O_3NO_2$	700,75
o-Nitrophenol	$C_6H_5ONO_2$	689,1
m-Nitrophenol	$C_6H_5ONO_2$	684,4
n-Nitrophenol	$C_6H_5ONO_2$	686,2
1,3,5-Trinitrobenzene	$C_6H_3(NO_2)_3$	663,7
1,2,4-Trinitrobenzene	$C_6H_3(NO_2)_3$	673,7
2-Amino-4,6-Dinitrophenol	$C_6H_2OHNH_2(NO_2)_2$	676,877
2,3,4,6-Tetranitroaniline	$C_6HNH_2(NO_2)_4$	655,036
2,4,6-Trinitroaniline	$C_6H_2NH_2(NO_2)_3$	673,249
o-Dinitrobenzene	$C_6H_4(NO_2)_2$	703,2
m-Dinitrobenzene	$C_6H_4(NO_2)_2$	694,7
n-Dinitrobenzene	$C_6H_4(NO_2)_2$	692,0
o-Nitrobenzoic acid	$C_7H_5O_2NO_2$	729,8
m-Nitrobenzoic acid	$C_7H_5O_2NO_2$	729,1
n-Nitrobenzoic acid	$C_7H_5O_2NO_2$	728,3
Nitrobenzene	$C_6H_5NO_2$	739,2
2-Methyl-2,3,3-Trinitrobutane	$C_5H_9(NO_2)_3$	700,46
2,4-Dinitroaniline	$C_6H_3NH_2(NO_2)_2$	718,859
2,4,6-Trinitrobenzaldehyde	$C_6H_2CHO(NO_2)_3$	729,106
1-Amino-2-Nitrobenzene	$C_6H_4NH_2NO_2$	765,8
1-Amino-3-Nitrobenzene	$C_6H_4NH_2NO_2$	765,2
1-Amino-4-Nitrobenzene	$C_6H_4NH_2NO_2$	761,0

Appendix 6 continued

Substance	Formula	Heat of combustion, kcal/mole
Dinitroneopentane	$C_5H_{10}(NO_2)_2$	746,91
2,4,6-Trinitro-m-cresol	$C_6HCH_3OH(NO_2)_3$	770
m-Nitrobenzaldehyde	$C_6H_4CHONO_2$	800,4
2,4,6-Trinitroanisole	$C_6H_2OCH_3(NO_2)_3$	734,300
2,4-Dinitroanisole	$C_6H_3OCH_3(NO_2)_2$	827,96
2,4,6-Trinitrotoluene	$C_7H_5(NO_2)_3$	816,9
Tetryl	$C_7H_5N(NO_2)_4$	836,5
2-Nitro-2-propylpropandiol-1,3	$C_6H_{13}O_2NO_2$	855,91
2-Nitro-2-isopropylpropandiol-1,3	$C_6H_{13}O_2NO_2$	859,36
2,4,6-Trinitro-N-methylaniline	$C_6H_2NHCH_3(NO_2)_3$	867,9
3,5-Dinitrotoluene	$C_7H_6(NO_2)_2$	853,0
2,4-Dinitrotoluene	$C_7H_6(NO_2)_2$	849
2,6-Dinitrotoluene	$C_7H_6(NO_2)_2$	853
2-Methyl-2,3,3-trinitropentane	$C_6H_{11}(NO_2)_3$	873,4
o-Nitrotoluene	$C_6H_4CH_3NO_2$	897,2
m-Nitrotoluene	$C_6H_4CH_3NO_2$	890,7
n-Nitrotoluene	$C_6H_4CH_3NO_2$	888,6
2,4-Dinitro-N-methylaniline	$C_6H_4CH_3N(NO_2)_2$	894,5
2,3-Dimethyl-2,3-dinitrobutane	$C_6H_{12}(NO_2)_2$	898,0
5-Nitro-o-toluidine	$C_6H_3CH_3NH_2NO_2$	910,4
3-Nitro-n-toluidine	$C_6H_3CH_3NH_2NO_2$	915,1
n-Nitro-N-methylaniline	$C_6H_4CH_3NHNO_2$	924,3
2,4,6-Trinitroprophenetole	$C_6H_2OC_2H_5(NO_2)_3$	945
m-β-Dinitrostyrene	$C_8H_6(NO_2)_2$	957,4
o-Nitroacetanilide	$C_8H_8NONO_2$	973,9
m-Nitroacetanilide	$C_8H_8NONO_2$	988,5
n-Nitroacetanilide	$C_8H_8NONO_2$	988,2

Appendix 6 continued

Substance	Formula	Heat of combustion, kcal/mole
2,4-Dinitrophenetole	$C_6H_3OC_2H_5(NO_2)_2$	950
o-Nitrophenetole	$C_8H_9ONO_2$	1021,2
m-Nitrophenetole	$C_8H_9ONO_2$	1009,2
n-Nitrophenetole	$C_8H_9ONO_2$	1006,0
2,4,6-Trinitrotolyl-3-methylnitramine	$C_8H_7N(NO_2)_4$	1009,3
o-Nitrocinnamic acid	$C_9H_7O_2NO_2$	999,0
m-Nitrocinnamic acid	$C_9H_7O_2NO_2$	995,6
n-Nitrocinnamic acid	$C_9H_7O_2NO_2$	996,5
ω-Nitrostyrene	$C_6H_5CHCH(NO_2)$	999,3
2,4,6-Trinitro-m-xylene	$C_6H(CH_3)_2(NO_2)_3$	971,643
2,4-Dinitro-1,3-dimethylbenzol	$C_6H_2(CH_3)_2(NO_2)_2$	1005
2,6-Dinitro-1,3-dimethylbenzol	$C_6H_2(CH_3)_2(NO_2)_2$	1000
1-Phenyl-2-nitropropene	$C_6H_5CHCNO_2CH_3$	1150,5
Trinitronapthalene	$C_{10}H_5(NO_2)_3$	1109,275
1,5-Dinitronapthalene	$C_{10}H_6(NO_2)_2$	1154,641
Dinitromesithylene	$C_9H_{10}(NO_2)_2$	1178,7
Nitromesithylene	$C_9H_{11}NO_2$	1204,7
Nitronapthalene	$C_{10}H_7NO_2$	1190,546
2-Methyl-2-nitro-1-phenylpropanol-1	$C_4H_8OC_6H_5NO_2$	1308,7
2-Methyl-2-nitro-3-phenylpropanol-1	$C_4H_8OC_6H_5NO_2$	1301,47
α-Nitrocamphor	$C_{10}H_{15}ONO_2$	1371,1
Hexanitrodiphenylamine	$C_{12}H_4NH(NO_2)_6$	1317,628
4,4-Dinitrohydrazobenzene	$(C_6H_4)_2(NH)_2(NO_2)_2$	1496,4
n-Nitrobenzyl	$C_{14}H_9O_2NH_2$	1600,9
N,N'-(Hexanitrodiphenyl)-ethylenedinitroamine	$C_{14}H_8N_{10}O_{16}$	1524
1,3,5-Cyclotrimethylenenitrosamine	$(CH_2NNO)_3$	555,3

APPENDIX 7

EQUILIBRIUM CONSTANTS K_{eq} FOR VARIOUS REACTIONS AND HEATS OF REACTION AT ABSOLUTE ZERO (ΔE_0^0 IS EXPRESSED IN KILOCALORIES)

Values are given in the form lg K_{eq}. For the reaction $A + B + \ldots \rightleftarrows C + D + \Delta E_0^0$, $K_{eq} = p_A p_B / p_C p_D$, where partial pressures p_A etc., are expressed in atm (tech). If in a reaction there participates a condensed phase, as for example in the case $C_{graphite} + 1/2\ O_2 \rightleftarrows CO$, that equilibrium constant is expressed in the form $K_{eq} = \sqrt{p_{O_2}}/p_{CO}$. Index "r" denotes (where necessary) the gaseous state.

Temperature, °K	$^1/_2H_2 + {^1/_2}Cl_2 \rightleftarrows HCl + 22,019$	$2Cl \rightleftarrows Cl_2 + 57,250$	$O_2 + O \rightleftarrows O_3 + 24,137$	$O_3 \rightleftarrows {^3/_2}O_2 + 34,513$	$HCN \rightleftarrows {^1/_2}H_2 + {^1/_2}N_2 + C_{graphite} + 31,380$	$NO + {^1/_2}O_2 \rightleftarrows NO_2 + 12,773$	$NO \rightleftarrows {^1/_2}O_2 + {^1/_2}N_2 + 21,477$	$2N \rightleftarrows N_2 + 170,240$	$CO + 3H_2 \rightleftarrows CH_4 + H_2O + 48,883$	$CO + H_2O \rightleftarrows CO_2 + H_2 + 9,680$	$CO + {^1/_2}O_2 \rightleftarrows CO_2 + 66,767$	$C_{graphite} + {^1/_2}O_2 \rightleftarrows CO + 27,202$	$C_r \rightleftarrows C_{graphite} + 170,390$	$OH + {^1/_2}H_2 \rightleftarrows H_2O + 67,107$	$H_2 + {^1/_2}O_2 \rightleftarrows H_2O + 57,107$	$2O \rightleftarrows O_2 + 117,172$	$2H \rightleftarrows H_2 + 103,240$	Temperature, °K
300	[illegible]	−36,67	−11,93	−28,29	−20,98	−6,42	−15,080	−118,66	−24,68	−4,95	−44,74	−23,98	−117,12	−46,29	−39,79	−80,09	−70,74	300
400	[illegible]	−26,08	−7,16	−22,15	−15,21	−3,94	−11,156	−87,47	−15,60	−3,17	−32,41	−19,13	−85,83	−33,91	−29,24	−58,51	−51,74	400
600	[illegible]	−15,44	−2,48	−15,98	−9,55	−1,44	−7,219	−56,21	−6,296	−1,44	−20,07	−14,34	−54,49	−21,47	−18,63	−36,86	−32,63	600
800	[illegible]	−10,07	−0,13	−12,89	−6,73	−0,18	−5,250	−40,52	−1,507	−0,61	−13,90	−11,93	−38,80	−15,22	−13,29	−25,99	−23,07	800
1000	[illegible]	−6,83	+1,29	−11,03	−5,04	+0,57	−4,088	−31,084	+1,625	−0,128	−10,199	−10,48	−29,38	−11,444	−10,060	−19,440	−17,288	1000
1200	[illegible]	−4,66	+2,24	−9,79	−3,92	+1,08	−3,279	−24,619	+3,395	+0,154	−7,742	−9,496	−23,10	−8,922	−7,896	−15,062	−13,410	1200
1400	[illegible]	−3,10	+2,92	−8,89	−3,12	+1,43	−2,717	−20,282	+4,810	+0,352	−5,992	−8,790	−18,62	−7,116	−6,344	−11,932	−10,627	1400
1600		−1,93	+3,42	−8,22	−2,53	+1,80	−2,294	−16,889	+5,873	+0,490	−4,084	−8,254	−15,26	−5,758	−5,175	−9,575	−8,530	1600
1800		−1,02	+3,82	−7,70	−2,07	+1,85	−1,986	−14,225	+6,70*	+0,591	−3,672	−7,829	−12,64	−4,760	−4,263	−7,740	−6,893	1800
2000		−0,28	+4,15	−7,29	−1,70	+2,07	−1,703	−12,106	+7,35*	+0,668	−2,863	−7,486	−10,567	−3,852	−3,531	−6,269	−5,579	2000
2200			+4,41	−6,95		+2,18	−1,488	−10,370	+7,88*	+0,725	−2,206	−7,201	−8,864	−3,158	−2,931	−5,064	−4,500	2200
2400			+4,63	−6,66		+2,29	−1,300	−8,922	+8,32*	+0,767	−1,662	−6,961	−7,446	−2,578	−2,429	−4,055	−3,598	2400
2600			+4,81	−6,42		+2,38	−1,157	−7,004		+0,800	−1,203	−6,759	−6,249	−2,087	−2,003	−3,206	−2,833	2600
2800			+4,97	−6,21		+2,46	−1,028	−6,640		+0,831	−0,807	−6,577	−5,223	−1,670	−1,638	−2,475	−2,176	2800
3000			+5,11	−6,08		+2,55	−0,915	−5,728		+0,853	−0,489	−6,418	−4,334	−1,302	−1,322	−1,840	−1,604	3000
3200			+5,28	−5,87			−0,817	−4,925		+0,871	−0,175	−6,273	−3,561	−0,983	−1,036	−1,285	−1,104	3200
3500			+5,39	−5,68			−0,682	−3,903		+0,894	+0,201	−6,094	−2,561	−0,577	−0,603	−0,571	−0,458	3500
4000			+5,60	−5,40			−0,536	−2,514		+0,920	+0,609	−5,841	−1,239	−0,035	−0,221	+0,382	+0,406	4000
4500			+5,76	−5,19			−0,345	−1,437		+0,928	+1,061	—	—	+0,392	+0,153	+1,125	+1,078	4500
5000			+5,89	−5,02			−0,298	−0,570		+0,937	+1,387	—	—	+0,799	+0,450	+1,719	+1,619	5000

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*Extrapolated.

APPENDIX 8

CHANGE OF INTERNAL ENERGY OF GASES AND GRAPHITE FROM 291° TO T° K IN kcal/mole*

Temperature in °K	H_2	O_2	N_2	CO	NO	OH	CO_2	H_2O	NH_3	Graphite C (solid)
291	0	0	0	0	0	0	0	0	0	0
300	0,045	0,045	0,045	0,045	0,046	0,046	0,062	0,054	0,06	0,0188
400	0,541	0,557	0,544	0,545	0,561	0,558	0,804	0,667	0,75	0,2063
500	1,041	1,089	1,047	1,052	1,085	1,064	1,633	1,300	1,51	0,5845
600	1,542	1,646	1,562	1,573	1,624	1,572	2,534	1,959	2,34	0,902
700	2,046	2,226	2,090	2,111	2,281	2,079	3,494	2,649	3,25	1,386
800	2,553	2,825	2,635	2,686	2,755	2,592	4,504	3,368	4,23	1,846
900	3,065	3,440	3,196	3,239	3,347	3,112	5,554	4,114	5,27	2,334
1000	3,591	4,069	3,771	3,826	3,954	3,696	6,639	4,889	6,39	2,839
1200	4,648	5,358	4,961	5,039	5,203	4,732	8,893	6,712	8,78	3,894
1400	5,752	6,682	6,199	6,295	6,492	5,869	11,233	8,239	11,36	5,006
1600	6,896	8,034	7,467	7,579	7,809	7,045	13,624	10,054	14,12	6,164
1800	8,081	9,407	8,762	8,889	9,141	8,261	16,087	11,955	17,01	
2000	9,302	10,803	10,076	10,218	10,491	9,509	18,570	13,924	20,01	8,544
2200	10,555	12,223	11,407	11,560	11,852	10,785	21,092	15,949	23,10	
2400	11,837	13,664	12,751	12,9[illegible]5	13,226	12,088	23,635	18,020	26,26	
2500	—	—	—	—	—	—	—	—	27,86	11,614
2600	13,145	15,124	14,105	14,278	14,609	13,413	26,202	20,128	29,49	
2800	14,477	16,608	15,469	15,649	16,001	14,758	28,786	22,267	32,77	
3000	15,829	18,112	16,939	17,029	17,397	16,120	31,382	24,466	36,08	14,794
3200	17,200	19,632	18,217	18,414	18,799	17,497	33,998	26,655	39,45	
3400	18,586	21,170	19,603	19,804	20,204	18,891	36,641	28,868	42,82	

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*Data for ammonia taken from D. Taylor's Dettonation in Condensed Explosives (Oxford at the Clarendon Press, 1952)

Appendix 8 continued

Temperature in °K	H_2	O_2	N_2	CO	NO	OH	CO_2	H_2O	NH_3	Graphite C (solid)
3500	—	—	—	—	—	—	—	—	44,51	18,034
3600	19,987	22,725	20,993	21,199	21,614	20,299	39,294	31,114	46,22	
3800	21,402	24,295	22,387	22,599	23,034	21,720	41,947	33,387	49,66	
4000	22,828	25,874	23,783	24,003	24,458	23,150	44,615	35,679	53,10	21,364
4200	24,267	27,470	25,187	25,408	25,888	24,598	47,296	37,959	56,58	
4400	25,714	29,078	26,595	26,818	27,324	26,054	49,991	40,243	60,05	
4600	27,173	30,697	28,007	28,234	28,768	27,524	52,687	42,537	63,55	
4800	28,640	32,318	29,418	29,657	30,219	29,009	55,379	44,839	67,05	
5000	30,118	33,943	30,840	30,971	31,679	30,497	58,118	47,182	70,57	

APPENDIX 8a

CHANGE OF INTERNAL ENERGY OF GASES FROM 291° TO T° K IN kcal/mole

Temperature °K	CH_4	HCN	Cl_2	HCl
291	0	0	0	0
300	0,062	0,059	0,056	0,045
400	0,773	0,763	0,687	0,542
500	1,616	1,536	1,341	1,042
600	2,602	2,363	2,012	1,547
700	3,725	3,239	2,692	2,060
800	4,976	4,156	3,378	2,584
900	6,314	5,112	4,069	3,121
1000	7,818	6,102	4,765	3,671
1100	9,379	7,120	5,464	4,234
1200	11,030	8,167	6,166	4,811
1300	12,761	9,241	6,870	5,401
1400	14,553	10,339	7,575	6,001
1500	16,394	11,458	8,284	6,732
1600	—	12,592	—	—
2000	—	17,288	—	—

APPENDIX 9

CHANGE IN INTERNAL ENERGY ΔE FOR CERTAIN SOLID COMPONENTS OF PRODUCTS OF EXPLOSION FROM 291° TO T° K IN kcal/mole

Temperature °K	Al_2O_3	NaCl	KCl	Na_2CO_3	K_2CO_3	MgO	CaO	BaO	TiO_2	S
291	0	0	0	0	0	0	0	0	0	0
300	0,16	0.11	0,10	0,25	0,28	0,08	0,09	0.08	0.12	0,03
400	2,2	1.3	1,3	3,1	3,3	1,1	1,2	1,2	1,6	0,38
500	4,5	2,6	2,6	6,1	6,4	1,3	2,3	2,4	3,0	0,74
600	7,1	3,9	3,9	9.2	9,4	3,1	3,6	3,6	4.6	1,1
700	9,7	5,2	5,3	12,1	12,6	4,3	4,9	4,8	6,3	1,4
800	12,6	6,7	6,6	15.2	15,8	5,4	6,2	6,2	7,9	1,7
900	15,5	8,1	8,0	18.4	18,9	6,6	7,6	7,6	9,8	2,1
1000	18,5	9,6	9,4	21,6	22,3	7,8	9,0	9,0	11,7	2,4
1100	21,6	18,3	17,3	24,7	25,6	8,9	10,5	10,5	13,7	2,7
1200	24,7	19,9	18,9	35,0	36,8	10,1	12,1	12,0	15,7	3,0
1300	28,1	21,4	20,5	38,3	40,1	11,4	13,7	13,7	17,9	3,3
1400	31,5	23,1	22,0	41,6	43,5	12,6	15,3	15,3	20,0	3,6
1500	34,9	24,3	23,7	45,0	47,0	13,8	17,0	16,9	22,3	3,9
1600	38,5	26,5	25,4	48,4	50,6	15,1	18,8	18,8	24,6	4,2
1700	42,2	28,3	27,8	51,8	53,9	16,4	20,6	20.5	27.1	4,5
1800	45,9	32.1	32,8	55,1	57,4	17,7	22,4	22,3	29,6	4,8
1900	49,8	37,0	37,8	58,5	60,7	19,0	24,3	24,3	32,2	5,1
2000	53,8	42,0	42,9	61,8	64,0	20,3	26,2	26,1	34,8	5,4
2100	57,8	46,9	48,3	65,1	67,3	21,6	28,2	28,1	48,9	5,7
2200	61,9	51,8	53,0	68,5	70,8	22,9	30,3	41,5	51,7	6,0
2300	66,1	56,7	53,1	71,8	74,1	24,3	32,3	43,8	54,6	6,3
2400	96,4	61,7	63,2	75,2	77,4	25,7	34,5	47,2	57,6	6,6
2500	100,9	66,6	68,2	78,6	80,7	27,1	36,7	50,4	60,6	6,9
2600	106,4	71,6	72,0	81,9	84,2	28,4	38,9	53,8	63,7	7,2
2700	109,9	76,5	72,6	84,8	87,5	29,8	41,2	57,0	66,8	7,5
2800	114,5	77,2	73,4	87,8	90,4	31,3	43,5	60,2	70,1	7,8
2900	119,3	77,9	74,1	90,9	93,4	32,7	45,9	63,6	73,5	8,1
3000	124,1	78,6	74,8	93,9	96,5	52,6	60,5	66,7	76,9	8,4
3100	129,1	79,3	75,5	96,8	99,4	54,1	63,0	70,2	80,3	8,7
3200	134,1	80,0	76,1	99,9	102,4	55,5	66,2	73,4	83,9	9,0
3300	139,5	80,7	76,9	102,9	105,5	57,0	69,5	76,6	88,1	9,3

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*Table prepared from data of P. Taverniev (Mémorial des Poudres, 1957).

Appendix 9 continued

Temperature °K	Al_2O_3	NaCl	KCl	Na_2CO_3	K_2CO_3	MgO	CaO	BaO	TiO_2	S
3400	145,4	81,4	77,6	105,8	108,4	58,5	72,8	80,0	93,9	9,7
3500	151,4	82,1	78,2	108,9	111,4	60,0	76,1	83,2	99,8	9,9
3600	157,5	82,8	79,0	111,9	114,4	61,5	79,4	86,4	105,6	10,2
3700	163,4	83,5	79,7	114,8	117,5	63,0	82,8	69,8	111,4	10,5
3800	169,4	84,2	80,4	117,8	120,4	64,6	86,1	93,0	117,3	10,8
3900	175,4	84,9	81,1	120,9	123,4	66,8	89,4	96,4	122,2	11,1
4000	181,3	85,6	81,7	123,9	126,5	70,8	92,7	99,6	128,8	11,4

APPENDIX 10

MOLAR VOLUMES OF CERTAIN SOLID INORGANIC SUBSTANCES, ENCOUNTERED IN PRODUCTS OF EXPLOSION

Substance	Molar volume l/mole	Substance	Molar volume l/mole
Borax (anhydrous, vitreous)	0.085	Potassium carbonate	0.0569
Silica (quartz)	0.0226	Sodium carbonate	0.0423
Aluminum oxide	0.0255	Potassium chloride	0.0376
Barium oxide	0.0278	Sodium chloride	0.027
Calcium oxide	0.0165		
Magnesium oxide	0.0109		

APPENDIX 11

VALUES OF SECOND VIRIAL COEFFICIENTS b OF GASIFORM PRODUCTS OF EXPLOSION AT HIGH TEMPERATURES

Gas	Coefficient b cm^3/mole	Gas	Coefficient b cm^3/mole
Ammonia	15.2	Nitric oxide	21.2
Carbon dioxide	37.0	Nitrogen	34.0
Carbon monoxide	33.0	Nitrous oxide	63.9
Hydrogen	14.0	Oxygen	30.5
Methane	37.0	Water vapor	7.9

APPENDIX 12

CERTAIN EXPLOSIVE TESTING METHODS AND INSTRUMENTS COVERED BY STATE ALL-UNION STANDARDS (GOST)

Definition chemical stability of nitroglycerine and nitroglycerine explosive by iodostarch sample

According to GOST 5772-51 the test is performed as follows.

In case of testing of nitroglycerine, about 5 ml are filtered for removal of excess water through a pure neutral paper filter directly into test tubes for testing up to the 2 ml mark.

In the case of plastic nitroglycerine explosives (dynamites), the test substance is cut with a horn knife into small pieces; weighings of 3.24 g are taken with a precision of 0.001 g and thoroughly mixed in a porcelain (in preference to a wooden) mortar with a wooden pestle with 6.48 g talc; then 3.24 g samples are taken with an accuracy within 0.01 g.

In the case of powered nitroglycerine explosives, the material is crushed in a porcelain (wooden) mortar with a wooden pestle without talc and 3.24 g samples taken with an accuracy within 0.01 g.

The prepared samples of the test substance are poured through funnels in thoroughly washed and dried test tubes, with care taken to prevent drops or particles of the substance from adhering to the walls of the test tubes. The test tubes are sealed with clean corks with hooks, on which have been suspended iodostarch papers, the lower half of which is moistened by a mixture of glycerine with water in a 1:1 ratio (by volume).

The suspension of the iodostarched papers and their wetting with the solution of glycerine is performed as follows.

The iodostarch papers are removed from a jar with a clean washed and dried forceps, place on a clean washed glass or cork plate, pierced with an awl and with the aid of forceps suspend on hook, placing the leaf of iodostarch paper in a vertical position; both lower corners of the paper are then moistened with a drop of the glycerine solution. The paper should evenly absorb the solution of glycerine up to half of its height, leaving a clear line between the moistened and dry parts. The test tube is closed with a cork in such a manner that the lower edge of paper is separated from the bottom of the test tube by 76 mm.

The prepared test tubes are lowered through holes in the cover of the bath into water heated to the required temperature; simultaneously with this, a stopwatch is set. The test tube is immersed in water in such a manner that the lower edge of the iodostarch paper is on one level with the outer surface of the bath cover. During the installation of the test tubes in the bath care is taken that the papers remain in a vertical position and do not touch the walls. Throughout the time of the test constant temperature is maintained in the bath through stirring.

The normal color standard is established in a standard bath in a special cavity. Observation conducted in reflected light.

The test is considered completed and the stop watch is shut off, when on the line, separating the dry part of iodostarch paper from the part, moistened with the aqueous solution of glycerine, there appears a line, identical in degree of color to the brown line of the normal color standard. The results of the tests are expressed in whole minutes (average results are not calculated).

The iodostarch test is performed in a special room, well ventilated, free of laboratory and factory gases. The walls of room must be colored with white oil paint. The room should be bright but protected from direct straight sunlight; the window panes should be of white frosted glass or in extreme cases, covered white fabric.

The heating of the test tubes with the test samples is done in a water bath, equipped with a stirrer and thermometer. In the cover of the bath are holes for the immersion of thermometer and test tubes in the water. The heating of the bath is produced by an electrical current with the aid of a closed electric heater or electric heater mounted in the bath. In the absence of electric power, the bath can be heated with the aid of stream or circulating water heated to the required temperature.

The bath should have uniform heating, assuring during the test maintenance of the same temperature in all test tubes with samples; the fluctuation of temperature must not exceed the limits ±0.5°C. In bath there should be a constant level of water, which must not reach the edges by 6 mm.

The bath is situated in such a manner that during the test, the leaves of the iodostarch paper are sufficiently illuminated by natural or artificial daylight. The test tubes have to be made of chemically durable colorless glass, not containing lead in their composition, and must not contain stones and waviness.

The length of the test tube should be 130-140 mm, the internal diameter 16-18 mm, and the thickness of walls 1-1.5 mm. The corks can be either glass, well fitted to the test tubes, with glass hooks soldered to their lower part, or rubber with through holes along the axis, in which glass hooks are inserted densely.

Hooks for suspending the iodostarch paper have a diameter of 4-5 mm, one end of them is distended and is bent in the form of a hook or equipped with a platinum wire, bent in the form of a hook.

Standard iodostarch papers are produced by special organizations. Every lot should be accompanied by a form, which should indicate the period of their serviceability. Iodostarch papers should be stored in a jar of stained glass with a fitted cork. During storage, the papers should be tested periodically for serviceability in the following way. A clean glass rod is used to apply to the iodostarch paper a single drop of a 10% aqueous solution of acetic acid. In the event of the immediate appearance of a brown (or blue) spot, the paper is rejected. Appearance of brown spot a minute or more after application of the drop of acetic acid solution does not provide cause for rejection of the paper, but indicates the necessity of using it as soon as possible with a check of serviceability before every test. Contact by hand with iodostarch paper is not allowed.

Iodostarched papers must be protected from the action of daylight, especially direct sunlight, since the sensitivity is strongly affected thereby.

Talc for the testing of dynamites is prepared as follows. Talc of the highest medical quality is subjected to multiple washing with tap water, distilled, water then (3-4 times) a weak solution of soda, and at last, distilled water. Washing is conducted until the dried, washed talc, placed in a test tube with iodostarch paper, upon heating for one hour at a temperature of 75°C will not give a positive reaction (absence brown line).

Definition of impact sensitivity of explosives

The method of determination and the instrument for it are described correspondingly in GOST 4545-48 and 2065-43.

According to the standard, the sensitivity of explosives to impact is their ability to decompose during the action of a freely falling weight falling from various heights.

The sensitivity criterion is the percentage of explosions from 25 parallel tests, as well as the minimum height of drop of the load, at which an explosion occurs.

The drop hammer, applied for testing explosives for impact sensitivity, roller and stamping instruments, and also loads have to correspond to GOST 2065-43. "Instrument for determination of impact sensitivity of pyrotechnic compositions."

Before testing, the sliding surface of the drop hammer is wiped with gauze moistened with ethyl alcohol, lubricated with a film of machine oil; the movement of the load of the drop hammer along the directrices is checked. The roller and stamping devices are washed with acetone or ethyl alcohol and wiped dry with gauze.

The tests are performed in the following way. An 0.05 g sample of the explosive, weighed with an accuracy up to 0.005 g is distributed evenly between the impact surfaces of the anvil and the head of the roller or stamping device, which then with the aid of a centering casing is placed on the drop hammer anvil.

The drop hammer load weighing 10 kg is set at a height of 250 mm and by pressing the discharge mechanism, the load is made to strike the head of the roller or stamping device. This determination repeated

25 times each time with a different roller or stamping device.

The tests are performed at room temperature.

The result of determination is expressed as a percentage of explosions in 25 parallel tests.

Note: If the experiment is accompanied by a sonic effect, a flash, smoke generation or carbonization of the tested material, it is assumed that an "explosion" has occurred. If the experiment is not accompanied by the above phenomena, it is assumed that a "misfire" has occurred.

If the percentage of explosions is equal to 100, the drop hammer of weight 10 kg is replaced by a load of weight 5 kg; the latter is set at a height of 250 mm and, as is described above, 25 parallel tests are performed. The result is expressed as a percentage of resulting explosions.

For checking the drop hammer, roller or stamping devices, a test of a standard explosive is performed.

As a standard in the test with a 10 kg load, tetryl according to GOST 626-41 which is doubly recrystallized from acetone is used; its crystals have to pass through a No. 25 sieve (size of holes 0.28 mm) and remain on a No. 32 sieve (dimension of holes 0.20 mm according to GOST 4403-48 "Silk fabrics for sieves"). The percentage of resulting explosions with a roller device should be equal to 48 ± 4%.

As a standard in the test of explosives with a 5 kg load hexogene, doubly recrystallized from acetone, with a magnitude of crystals given above for tetryl is used. The percentage of explosions on a roller device also should be equal to 48 ± 4%.

Tests of explosives for impact sensitivity are considered valid only in the case when the results of tests of the standard explosive correspond to the above requirements.

The impact sensitivity of industrial explosives is determined by using stamping devices and a load of weight 2 kg. The sensitivity criterion is the minimum height of drop of the load, at which there occurs an explosion. As a standard apply trotyl according to GOST 3471-46 is used; the height of drop of the load 2 kg should be equal to 1000 mm.

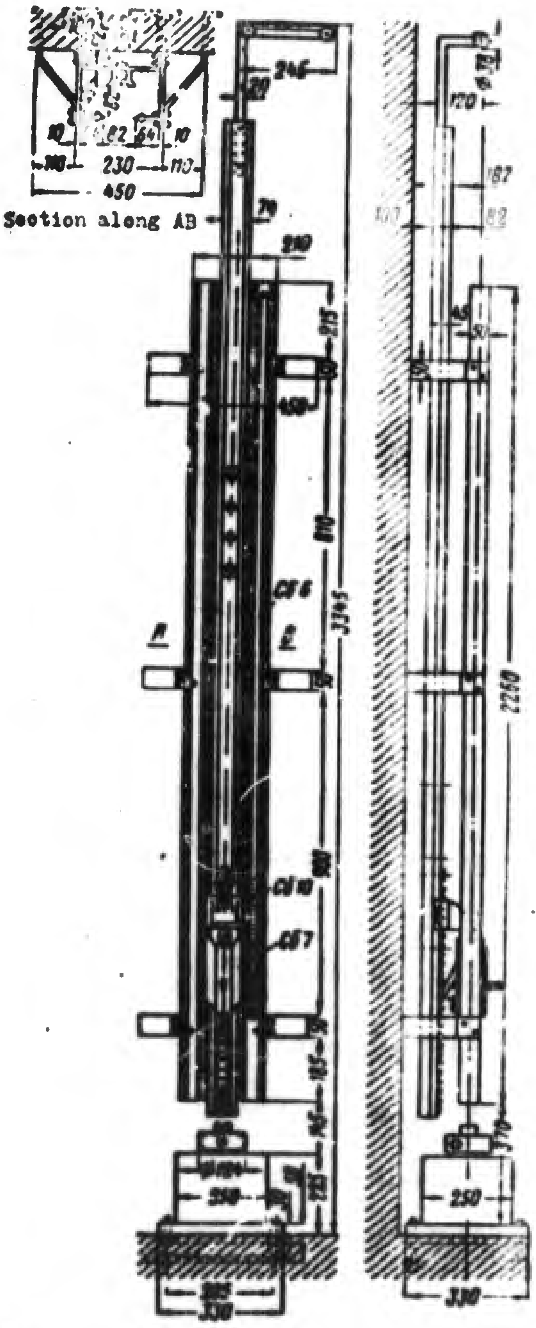
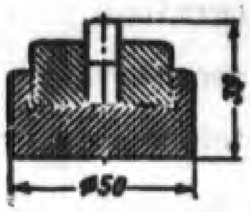


Fig. 1. Kast drop hammer.
[Cб = Sb (unidentified)]

After completion of the tests, the roller of stamping devices are washed with acetone or ethyl alcohol, wiped dry with gauze, and lubricated with machine oil.

If the test involves a liquid explosive, a sample (2 drops) is placed not directly in the roller device, but in a German silver capsule cap of the following dimensions: diameter 5.95 mm, height ~3.75 mm, and thickness of walls 0.15-0.20 mm. The cap is placed in the roller device between the head and anvil. The tests conduct just as for solid explosives.

The device for determination of the impact sensitivity consists of the Kast drop hammer (Fig. 1) and a roller attachment with a centering casing. The drop hammer load, suspended on metallic cable, is equipped with an attachment, by means of which it may be fixed at a given height, indicated on a scale.



.Fig. 2. Roller attachment.

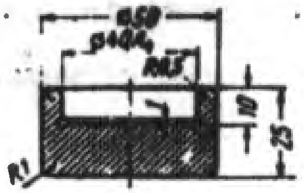


Fig. 3. Steel pan.

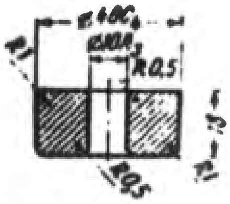


Fig. 4. Directing bushing.

The roller attachment (Fig. 2), mounted on the base of the drop hammer with the aid of the centering casing (Fig. 6), consits of a steel pan (Fig. 3), directing bushing (Fig. 4) and of two rollers inserted in the latter (Fig. 5). Instead of the roller attachment it is possible to use a Kast stamper with centering casing.

.Fig. 5. Roller.

The rollers used as the drop hammer and anvil must conform to the following requirements:

a) According to the quality of material and heat treatment the rollers have to satisfy the requirements, imposed on cylindrical rollers of ballbearing factories;

b) The cylindrical and butt end surfaces have to be thoroughly polished. Quality of treatment should correspond to that of standard parts.

The drop hammer load should have a weight 10,000 ± 10 g and should freely slip between the guides. Scale on the drop hammer rule which permits the setting of the necessary height of rise of load, should be of a length not less than 100 cm, with divisions of 1 mm. The setting of the load at the required height should be assured by an attachment with accuracy up to 1 mm.

After the impact of the load against the roller device and rebound, impact should not be repeated.

In the mounting of the roller attachment on the base of the drop

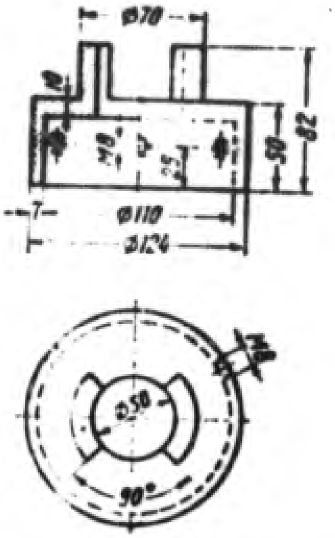


Fig. 6. Centering casing.

hammer it is necessary to assure exact centering of the roller device with respect to the load.

The base of the drop hammer is mounted on a massive foundation, while the guides are fixed in a vertical position.

Determination of speed of detonation of explosives by Dautriche

According to GOST 3250-58 determination is performed as follows.

The tested explosive is placed in a metallic shell (seamless tube), closed off on both sides with screwed caps, in one of which is a hole for the detonator capsule. The metallic shell for the charge should be prepared in accordance with Fig. 7, and the cap of the shell — with Fig. 8; the hole for the detonator capsule is present in just one of the caps.

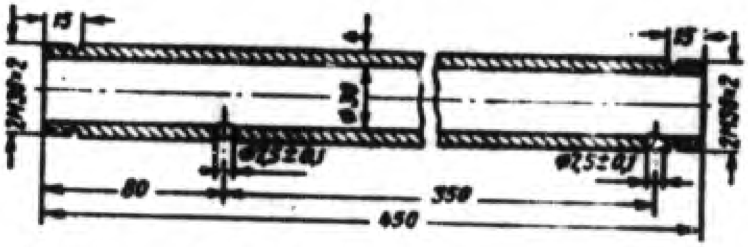


Fig. 7. Metallic shell for charge.

The density of the tested explosive should be uniform throughout the length of the charge, enclosed in the shell. Low-density charges (ρ = 1.1 and less) are prepared by uniform loading of the tested explosive in the shell with a wooden punch, in portions of 40 g in such a way that every portion takes up an identical height in the tube.

The height of loading of one portion of the substance in the tube (h) is calculated with the formula

$$h = \frac{4 \cdot G \cdot 1000}{\pi d^2 \rho}.$$

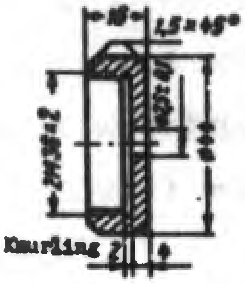


Fig. 8. Cap of shell.

where G is the weight of one portion of explosive in g; d is the inside diameter of the shell in mm; ρ is the required density of the explosive in g/cm^3. High-density charges (ρ = 1.2 and more) are made up of separate pressed tablets of height 40 ± 0.2 mm.

The weight G of one tablet in g is calculated from the formula

$$G=\frac{\pi d^2 h\rho}{4\cdot 1000},$$

where d is the internal diameter of the pressform in mm, which should be within the limits 29 ± 0.2; h is the height of the tablet in mm; ρ is the required density of the explosive in g/cm^3.

The density of the tested explosive is checked with not less than 20% of the tablets.

<u>Note</u>: The check of tablet density is performed with the aid of a densitometer or by means of an actual calculation from the real weight of the tablet and size measurement data under the condition that the tablet does not have defects, chipping, cracks, deep furrows, crumbling dents, etc.

For initiation of the tested explosive, a tetryl detonator is used; it has a cavity for the detonator capsule of depth 15 mm and diameter 7.5 mm. The density of the tetryl detonator should be 1.5-1.6 g/cm^3, the diameter 29 mm, and weight 30 g.

In the loading of the tube, the tetryl detonator is placed end to end with the charge, covered with cardboard packing with holes; the cap is then screwed on (see Fig. 8). Cardboard packing is also placed under the holeless cap at the other end.

The detonating fuse, used in the test, should have a uniform speed of detonation. The speed of detonation of the fuse is determined with the aid of an oscillograph of photochronograph, as the average of four determinations; this is done by removing two samples from one end of the fuse coil and two samples from the other end.

The speed of detonation of the fuse should be not less 6500 m/sec; the scattering of speeds must not exceed ±1.5% of the average value.

In the determination of the speed of detonation of explosives, lying within limits of 2500 m/sec and above, two sections of the detonating fuse are taken – one of length 1500 ± 0.5 mm, the second of length 1000 ± 0.5 mm. If the expected speed of detonation of the tested explosive less than 2500 m/sec, then it is necessary to decrease length of section of charge, on which is determined the speed of detonation, to 200 mm or to increase the long section of the detonating fuse to 2200 mm.

The fixing plate, marking the meeting of shock waves, passing over the detonating fuse, is made from brass in accordince with Fig. 9, by the 9th class of accuracy. On the fixing plate, a distance 500 mm from each other are drawn two lines A and B.

The cushion plate on which the fixing plate is mounted, is made of steel in accordance with Fig. 10 by the 9th class of accuracy.

The protective tube, which serves to protect the fixing system from fragments during the detonation of the charge, is constructed in accordance with Fig. 11.

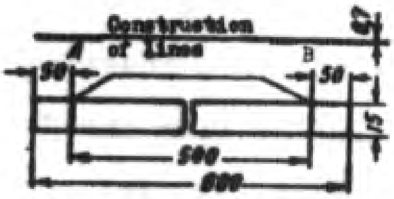


Fig. 9. Fixing plate.

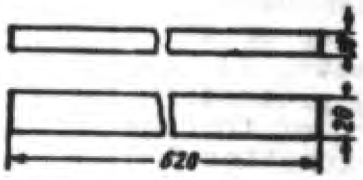
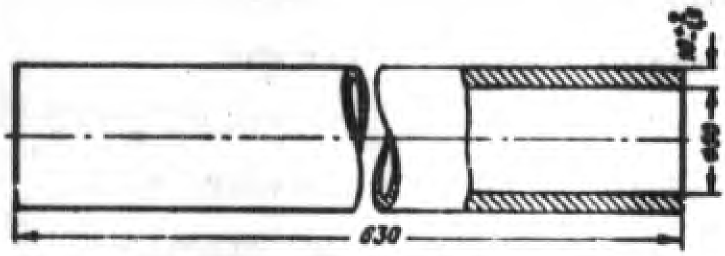


Fig. 10. Cushion plate.

The test is conducted in the following way: with a nonferrous

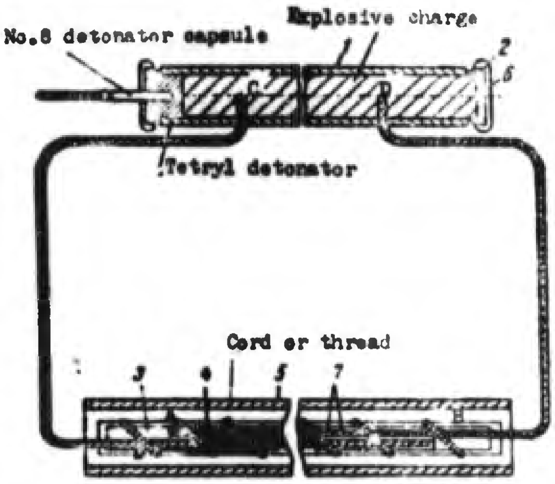


.Fig. 11. Protective tube.

metal drill, through the two holes, located in the shell of the charge, cavities of a depth 15 ± 1 mm and diameter 6-6.5 mm are drilled in the charge.

From the detonating fuse coil, sections are measured with vernier calipers cut with sharp knife on a board.

On the cushion plate is placed the fixing plate with constructed lines A and B. On the latter are placed the sections of the detonating cord in such a manner that one of the ends of the short fuse strictly coincides with line A, and one of ends of long cord – with line B, as is shown on Fig. 12.



.Fig. 12. Diagram of device for determination of speed of detonation. 1) charge shell (seamless tube 38 × × 4), 2) cap of shell, 3) fixing plate, 4) cushion plate, 5) protective tube, 6) padding of thickness 1.5 mm, 7) detonating fuse.

The entire system is secured with cords or thick threads.

The fixing system secured in this way is inserted in the protective tube in such a manner that the free ends of the detonating cord emerge from it on both sides (Fig. 12).

The end of the long section of the detonating fuse are inserted into the first (measuring from the detonator) charge of charge, and the short – into the second, to a depth of 15 mm.

The protective tube and charge have to be placed in such a manner that the detonating cord does not touch the external walls of the charge and is not sharply bent.

Note: With a speed of detonation of less than 2500 m/sec, misfires of the detonating fuse are possible due to the insufficiency of the initiating impulse. In this case to ends of detonating fuse, inserted in the cavities of the charge, are attached by threads No. 8 detonator capsules, which are inserted with the open end in the cavity of the charge of the tested explosive.

An overall diagram of the assembly of parts and elements, used in the determination of the speed of detonation of explosives, is shown on Fig. 12.

With help of the No. 8 detonator capsule with a firewire cord or with the aid of an electrodetonator, inserted in the detonator of charge through a hole in the cap, the charge is exploded.

The explosion is produced in an armorpit, on a polygon or in the ground at a depth of 1 m from the surface. The appropriate rules of safety engineering are observed.

After the explosion the fixing plate is removed from the protective tube and measured with the aid of vernier calipers with an accuracy up to 0.2 mm, the distance from the center of its mark (point of meeting of detonation) to lines A and B.

The speed of detonation D in m/sec is calculated from the formula

$$D = \frac{D_{\text{ШН}} \cdot l}{l_1 - l_2},$$

[ШН = fu = fuse]

where D_{fu} is the speed of detonation of the detonating fuse in m/sec;

l is the length of the section of charge, on which is determined the speed of detonation (distance CD on Fig. 12), expressed in m;

l_1 is the distance from center of mark, obtained on the fixing plate, up to the start of the long section of cord (distance from the center of the mark to point A plus length of section AC), expressed in m;

l_2 is the distance from center of the mark, obtained on the fixing plate, up to the start of the short section of cord (distance from center of the mark to point B plus length of section BD), expressed in m.

For every investigated sample, two parallel determinations are performed, from the results of which the arithmetic mean is computed.

The deviation of the magnitudes of speeds of detonation in separate determinations from the arithmetic mean does not have to exceed ±1.5%.

For control of correctness of determination, periodical measurements are made of the speed of detonation of trotyl (with a charge density 1.55), which with observance of all above-indicated conditions of test should be 6800 ± 150 m/sec.

Definition of high-explosive action of explosives in lead bomb

The lead bomb according to GOST 4546-48 should satisfy the following requirements:

a) have the form of a cylinder with a closed channel along the axis;

b) the dimensions of the bomb must be:

height	200 ± 2 mm
diameter	200 ± 2 mm
depth of channel	125 ± 2 mm
diameter of channel	25 ± 0.5 mm

c) the bombs are cast from lead according to GOST 3778-56 or from lead, obtained by remelting of used bombs. The casting of bombs is performed in a single operation at a temperature 390-400°C. From bombs, poured from one melt of lead, a run of bombs is produced. The checking of the quality of a run of lead bombs is performed with a standard explosive — trotyl recrystallized from alcohol, having temperature of hardening to recrystallization not less than 80.2°C (GOST 3471-46); the expansion should be within 285 ± 7 ml; otherwise, the bombs of the run are not used for testing. The quantity of lead bombs, subjected to checking with the standard explosive, should be not less two from every run;

d) the bottom of the bomb must not have a shrinkage cavity, and the surface should be monolithic, without scaling. Sinks in the channel are not allowed;

e) ready bombs are used in tests not earlier than after 48 hours after casting;

f) for every determination, a lead bomb, not formerly in use is employed.

Used lead bombs are remelted not more than 10 times. In the casting of bombs from fresh lead, an addition of not more than 50% lead from bombs, formerly in use is allowed.

The quartz sand used as filler should be air-dry and should pass through sieve with a No. 07 grid and to remain on a sieve with a No. 042 grid according to GOST 3584-53.

The cartridge case is made of imitation parchment, cut to pattern, corresponding to an orthogonal trapezoid with dimensions 150 × 120 × × 70 mm. The pattern-cut sheet is wound on a wooden cylinder of diameter 24 mm in such a manner so that the lower base of trapezoid projects over the end of the cylinder by 15-20 mm. The projecting part is bent and glued, forming the bottom of the case.

For initiation of the explosion, a No. 8 fulminating mercury-tetryl detonator capsule in a paper shell is used; the capsule is connected to a 30-35 cm length of Bickford (safety) fuse or a No. 8 electrodetonator.

The cardboard wad is made of cardboard of thickness 1.0-1.5 mm;

the external diameter of the wad is 24 mm; the diameter of the hole is 7.5 mm.

The test is performed as follows. A 10 ± 0.01 g sample of the explosive is placed in a shell case. Over the explosive insert is placed the cardboard wad. In special matrix of diameter 24.5 ± 0.1 mm with the aid of bronze punch of diameter 24 ± 0.2 mm, having on its end a flange in the form of a detonator capsule (diameter 7 mm and length 12 mm), the explosive is pressed to obtain a density, used under exploitational conditions, and in comparative tests — to a density, equal to 1 g/cm^3. In the cavity of the cartridge is inserted a detonator capsule.

The charge thus prepared is inserted in the bomb channel, the volume of which has been measured, and carefully tamped down with a small wooden stick to the bottom. The remaining free space in the channel of the bomb is covered with quartz sand (without packing, to the level of the upper end of the bomb channel). The explosion is then produced.

After the explosion, the bomb channel is cleaned with a hair rag-bolt and the contents are removed by overturning the bomb. The expansion of the bomb channel, due to the explosion is measured with water with the aid of a measuring cylinder of 500 ml capacity. The difference between the measured volume of the bomb channel after explosion and the volume of channel prior to explosion expresses the numerical value of the high-explosive action of the tested explosive.

The high-explosive action is expressed as the arithmetic mean of two parallel determinations, the deviation between which must not be more than 10 ml.

If the test is performed at a temperature of the bomb, different from +15°C, then a correction is introduced into the result in accordance with the following table:

Temperature of bomb, °C	−30	−25	−20	−15	−10	−5	0	+5	+10	+15	+20	+25	+30
Correction in % of measured expansion	+18	+16	+14	+12	+10	+7	+5	+3,5	+2,0	0,0	−2,0	−4,0	−6,0

The final result round to the nearest integer.

Definition of brisance of explosives by test by explosion on lead cylinder

According to GOST 5984-51, lead cylinders are cast in forms with a polished inner surface from lead according to GOST 3778-56. Every cylinder is cast in a single operation at a temperature 400 ± 10°C. It is permissible to produce lead cylinders by melting of used cylinders.

The butt end surfaces of lead cylinders have to be parallel and mechanically treated. Roughness of treatment should correspond to $\nabla 4$. The dimensions of the lead cylinder must be: height 60 ± 0.5 mm diameter 40 ± 0.2 mm.

The lead cylinders are produced in individual runs. A run may consist only of cylinders, poured from a single melt of lead. Every run is assigned its own number and accompained by all specifications.

Every party of cylinders is tested for rigidity of lead by compression of cylinders during the detonation of a standard sample of trotyl. The standard sample is trotyl, satisfying requirements of GOST 3471-46 and then recrystallized from ethyl alcohol with crystals, passing through a No. 9 sieve (dimension of holes 0.16 mm) and remaining on a No. 21 sieve (dimension of holes 0.08 mm) (GOST 4403-56).

To check the rigidity of lead, from every run of cylinders are moved not less than 2% of the cylinders, but not less than 4 with all runs.

Magnitude of compression is determined through measurement of height of cylinders before and after tests in four diametrically opposite points with an accuracy up to 0.1 mm, as is shown on Fig. 13; as the result of measurement of cylinder is taken the arithmetic mean of four measurements, rounded off to 0.1 mm. The difference between the initial height of the lead cylinder and the height after compression expressed in millimeters, numerically represents the magnitude of compression.

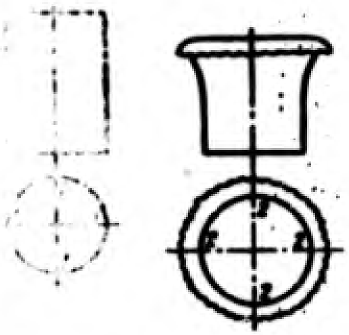


Fig. 13. Diagram of measurement of lead cylinder before explosion and after it [illegible]).

The final result in the compression of lead cylinders, by means of detonation of a standard sample of trotyl is determined as the arithmetic mean of the results of tests of four samples of a given run.

The run of cylinders is considered suitable, if during the testing of standard trotyl, with a charge of density 1 g/cm^3, the compression of lead cylinders constitutes 16.5 ± 0.5 mm.

The steel disk, placed in the test over the lead cylinder, should have the following dimensions: height 10 ± 0.2 mm, diameter 41 ± 0.2 mm. Treatment with ∇6 disk.

The hardness of the steel disk should be 150-200 according to Brinell. It is possible to have repeated application of the steel disk after control measurement for conformity to dimensions.

The steel plate, on which the tests are conducted, should have thickness not less than 20 mm and a diameter or length of side not less than 200 mm. The treatment of the side of the plate, on which is placed the lead cylinder is $\nabla 4$. The plate should have four hooks for bracing the charge.

The case for the explosive is prepared from a sheet of dense paper of thickness 0.15-0.20 mm with dimensions 65 × 150 mm. From the cut sheet of paper is glued a cylinder, having an internal diameter of 40 mm. To the cylinder is glued a bottom of the same paper, for which purpose is cut a circle of diameter 60 mm; the edges of the circle are incised to a diameter of 40 mm; the cut edges are bent onto the outer part of case and glued on to it.

The cardboard circle with which closes the charge in the case, is made of cardboard of thickness 1.3-2.0 mm. In the center of the circle is made a hole for the introduction of the detonator capsule.

The outer diameter of the circle should be 38-39 mm; the diameter of the hole in it 7.5 mm.

For centering the detonator capsule the use of a plywood circle of thickness about 5 mm is allowed.

The determination is performed as follows.

50 ± 0.1 g of the tested explosive is placed in a paper case and close from above with the cardboard circle.

In a special matrix, having a forming stamp, the charge is compressed to a density of 1 g/cm^3. Industrial explosives are tested for densities, given in the corresponding GOST's or specifications.

Along the axis of the explosive charge should be a channel for the detonator capsule (or electrodetonator) of diameter 7.5 mm and length 25 mm.

In the preparation of a charge for testing in a cavity, under the detonator capsule is inserted a wooden cylinder of diameter 7.5 mm and length 50 mm. Detonation is effected with a No. 8 detonator capsule (fulminating mercury-tetryl) or No. 8 electrodetonator in paper shells. The detonator capsule is inserted in the cartridge cavity only at the detonation site.

The explosion is produced either by the ignition of free end of a firewire fuse either (in the case of the electrodetonator) with the aid of an electrical current. The No. 8 detonator capsule is connected with the section of firewire fuse of length 30-35 cm according to existing rules of safety engineering. Capsule-detonators are best taken from the same lot, which was used in the test of the lead cylinder lot.

The steel plate is placed horizontally on a concrete foundation or some on other solid base. On the plate is placed a lead cylinder, over which is placed the steel disk. On the disk is placed the case with the charge of test explosive and inserted detonator capsule.

Fixed system is centered and strengthened on a plate, after which the detonation is produced. Two parallel tests (explosion) are performed, from results of which the arithmetic mean is computed.

A divergence between parallel tests of not more than 1.0 mm is allowed. If unsatisfactory results are obtained, repeated tests of three new samples are performed. If unsatisfactory results appear in repeated tests, the run of explosive is considered to have failed the tests.

Testing of safety explosives for safety with respect to the ignition of the methane-air and dust-air mixture in an experimental drift

According to GOST 7140-54, the tests are performed as follows.

The tests are performed on safety explosives in cartridges 31-32 mm in diameter and density 1.0-1.15 g/cm^3. The test for safety with respect to the ignition of the methane-air mixture is performed with a charge of 600 g, and the ignition of coal dust with a charge of 700 g.

The test of explosives are performed in the same cartridge sizes, in which they are manufactured. The compressed powdered explosive in cartridges should be crushed before testing.

The average sample of explosives is taken from 2% of the boxes in a lot; not less than one packet or package is taken from each box. The samples for testing of explosives for safety with respect to the ignition of the methane-air mixture and coal dust are taken from the average sample. The total weight of the sample should be not less than 4 kg.

In the testing of safety explosives with respect to the ignition of the methane-air mixture 3 experiments are performed for each lot, while in testing for ignition of coal dust, 2 experiments are performed for each lot, of which one experiment does not involve pouring of coal dust into channel of mortar and one experiment with pouring of 100 g of dust into the mortar channel. The basic mass of coal dust is placed in the free space between charge and mouth of mortar.

In case of ignition of the methane-air mixture or hard coal dust, repeated tests are performed.

In repeat tests, samples are taken from a double quantity of boxes and double the number of experiments are performed. If in repeat tests unsatisfactory results are obtained even with respect to one indicator (gas or dust), the test for the other index is not performed, and the lot is rejected.

Every manufacturing plant not less than once a year dispatches the the Makeyevskiy Scientific Research Institute of Mining Safety (MakNII) samples from their gross output of all sorts of safety explosives in an amount of not less than 60 kg of every sample for control testing.

Tests of experimental lots of new and experimental gross lots (permanent) of safety explosives for safety from ignition of methane-air mixture at the MakNII are performed at the rate of 10 experiments for each lot; tests of safety from ignition of coal dust – from an experimental lot of a new safety explosive are conducted at the rate of 10 experiments, per lot of which 5 experiments are without pouring of coal dust into mortar channel and 5 experiments with pouring of 100 g of coal dust into mortar channel.

Tests for safety with respect to the ignition of methane are performed in the following way. First clay stemming is prepared by drying plastic clay to content of moisture of not more than 5%; the stemming is prepared from it by mixing four parts by weight of clay with one part by weight of water. The mixture is thoroughly mixed to obtain a uniform dough-like mass.

50-55 g of the prepared clay with a 20-25% moisture content is placed in a device for the production of stemming (Fig. 14), consisting of a metallic cylinder or slightly truncated cone (preferably of stainless steel) 1, header 2, and wooden stamp 3. With the aid of the stamp the clay is packed into a flat cake to a thickness 10^{+1} mm. The upper edges of the stamp have to be on the level of the height of the cylinder. Then the header is carefully removed from the cylinder and the stamp presses it into a flat clay cake.

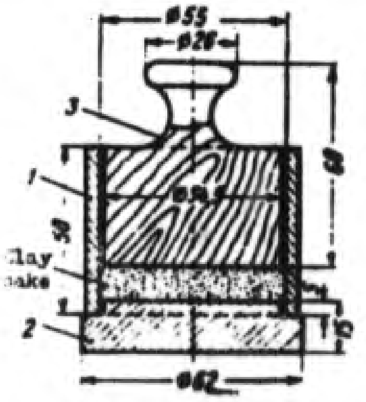


Fig. 14. Device for manufacture of stemming.

In case of adhesion of the clay to the walls of the cylinder of its wall is first slightly lubricated with machine oil to a height of 1.5-2 cm.

The test in the experimental drift is performed as follows.

With the aid of a diaphragm made of a material, not permeable to the methane-air mixture, an explosive chamber of capacity 10-11 m^3 is partitioned off in the experimental drift.

The cartridges of the tested explosive are placed in the mortar consecutively, one after another, end to end in one row in such a manner that the resulting charge rests against the bottom of the channel, while the cartridge next to the mouth of the mortar is at a distance of not less than 5 cm from the face of the mortar (Fig. 15).

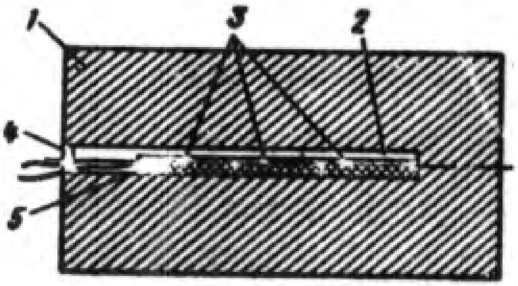


Fig. 15. Location of cartridges of explosive in mortar. 1) mortar body, 2) mortar channel, 3) explosive cartridges, 4) clay stemming, 5) electrodetonator.

In this cartridge is inserted a No. 8 fulminating mercury-tetryl electrodetonator of the instantaneous action type in a paper or copper shell, with the latter inserted to its entire length.

The bottom part of the electrodetonator should be directed in the direction of the bottom of the mortar channel. Then the mouth of the channel is closed off flush with the internal stemming made of plastic clay, which slightly pressed to the walls of the mortar channel.

The charged mortar is rolled close to the hatch of explosive chamber of the drift in such a manner so that the stemming does not drop out.

Into the chamber is admitted gas, containing not less than 90% methane and no hydrogen, in such a quantity, that the concentration of methane constitutes 8-10% (by volume). Before detonating the methane-air mixture, is mixed with a ventilator or mixer and the content of methane determined with the aid of a Seger pipette or gas analyzer.

The temperature of the methane-air mixture in the chamber should be from -10 to +30°C.

The determination of the methane content in the Seger pipette is produced in the following way. The Seger pipette, filled with water, is connected to a carbine, on the pipe of the drift, and the upper valve opened; then the lower valve of the pipette is opened. When the last drop of water in pipette has passed through the hole in the lower valve; it is closed, then the upper valve of the pipette is opened. The combustion of gas is produced by an electric spark.

Pipette lower into a vessel with a 15-20% solution of sodium chloride in such a way, that approximately one fifth of the pipette in the solution; then the lower valve of the pipette is opened. Upon the expiration 10-15 sec, the valve is closed, the pipette removed from the solution, agitated several times, and once again the pipette is lowered into the vessel. Directly in the solution the pipette valve is opened again and the pipette is set in such a way, that the height of the solution in the pipette is on the level of the solution in vessel. The valve is closed, the pipette removed from the vessel and the volume of solution entering the pipette is measured with the aid of a graduated cylinder.

The content of methane X as a percentage is calculated from the formula

$$X = \frac{v \cdot 100}{2 \cdot v_1},$$

where v is the volume of solution, entering the pipette, in ml;

v_1 is the volume of pipette in ml.

The determination of the methane content with help of the gas analyzer is performed according to the gas analyzer scale indications.

The correctness of gas analyzer readings is checked with the aid of a Seger pipette periodically, not less often than once a week.

Tested charges of safety explosives are detonated only by explosive machines, licensed for use in mines, dangerous with respect to gas and dust.

Safety explosives are considered as having withstood the test for ignition safety, if charge of 600 g in the above conditions does not ignite the methane-air mixture. The weight of the charge is composed of the weight of the cartridge as indicated without additional weighing. If in tests in a mortar channel or explosive chamber there is a residue of exploding material remaining, it is considered as not having withstood the test, even if ignition of the gas does not occur.

The safety with respect to coal dust is performed in the following way.

The coal dust used in the test is obtained by crushing of coal from the "Makeyevskiy" layer of the "Yushnaya Chaykino" mine with a content of volatile materials not more than 29-35%, ashes — not more than 9%, moisture — not more than 2%, or some other coal, containing the same quantity of volatile materials, ashes, and moisture.

Carbon should be crushed to such a degree, that the residue on a No. 15 sieve (according to GOST 4403-56 size of holes 0.5 mm) in the test does not exceed 10% and that through a No. 76 sieve (according to GOST 4403-56, size of holes 0.071 mm) passes not less than 50% of the dust.

The coal dust in the experimental drift is pulverized with the aid of a spray mortar with a channel of length 500-700 mm and diameter 150-220 mm. The mortar is set at an angle of 20° with respect to the horizontal axis of the drift at distances of:

- 11.5 m from the bottom of the drift with a drift diameter of 1500 mm;
- 10 m from the bottom of the drift with a drift diameter of 1600 mm;
- 8 m from the bottom of the drift with a drift diameter of 1600 mm.

In the spray mortar is placed a charge of the tested explosive of weight 50 ± 5 g with a No. 8 fulminating mercury-tetryl electrodetonator in a paper or copper shell; over this is poured 6 ± 0.1 kg of coal dust.

In the mortar is placed a charge of the tested explosive of weight 700 g placing the cartridges and electrodetonator just as in the test for the methane-air mixture.

In case of test explosives in cartridges of weight 200 g one half of a cartridge is taken for the test; this is placed between the first and second cartridges, considering as the first the cartridge, located nearer to the mouth of the mortar. In the case of testing of explosives in cartridges of weight 300 g, one third of the cartridge is taken and placed just as indicated for the cartridge of weight 200 g.

In first cartridge is placed a No. 8 fulminating mercury-tetryl electrodetonator in paper or copper shell throughout the length of the electrodetonator. The atomization of the coal dust from the spray mortar is performed along the drift 5-10 sec before the explosion of the test charge.

Safety explosives are considered as having passed the test for coal dust, a 700 g charge under above conditions did not ignite the coal dust.

If during the tests the mortar channel or explosive chamber is found to contain a residue of unexploded explosive, it is considered as having failed the test, even if ignition of dust did not occur.

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