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FOREIGN TECHNOLOGY DIVISION

AIR FORCE SYSTEMS COMMAND

FUNDAMENTALS OF THEORY AND CALCULATION OF LIQUID-PROPELLANT ROCKET ENGINES

Volumes I-III

by

A. P. Vasil'yev, V. M. Kudryavtsev, et al.

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Vol I of 3

EDITED MACHINE TRANSLATION

FUNDAMENTALS OF THEORY AND CALCULATION OF LIQUID-PROPELLANT ROCKET ENGINES

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By: A. P. Vasil'yev, V. M. Kudryavtsev, et al.

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ABSTRACT

PURPOSE AND COVERAGE: Theoretical and design principles of liquid rocket engines are presented. Extensive coverage is given to processes taking place in the combustion chamber, calculations of mixing systems, the cooling and contour calculation of the nozzles, calculation and selection of optimal parameters, turbopump and fuel feed pressurization systems, generation of the working medium for the turbine and fuel feed pressurization system, design and integration of pneumohydraulic systems for liquid rocket engines, calculation methods and selection of a liquid rocket engine parameters with a closed generation circuit of the working medium for the turbine. Basic theoretical and design principles of processes taking place in different types of liquid rocket engines are presented. The operation of main subsystems and the calculation of their characteristics are discussed. The presented information included the selection of liquid rocket engine systems, overall performance of the subsystems, and the method of calculating optimal parameters. The book is intended for students specializing in rocket engines. It may be of interest to engineers working in the rocket technology field. The book was written with the assumption that the students have previous knowledge of thermodynamics, gas dynamics, hydraulics, and heat transfer. Soviet and foreign literature on rocket engines was used in writing this monograph. 864 equations, 268 figures, 12 tables.

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U. S. BOARD ON GEOGRAPHIC NAMES TRANSLITERATION SYSTEM

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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

VOLUME I

ANNOTATION

In the book there are discussed fundamentals of theory and calculation of liquid-propellant rocket engines (ZhRD). Much emphasis is placed on questions of the course of the operating process in the combustion chamber, calculations of mixer elements, cooling and profiling of combustion chamber nozzles, calculations and selection of optimum parameters, turbopump and pressure fuel feed systems, calculation of means of generation of working medium for turbine and pressure fuel feed system, design and composition of pneumatic and hydraulic circuits of liquid-propellant rocket engines, specific character of calculation and selection of parameters of liquid-propellant rocket engines with a closed system of generation of working substance for turbine. In the book there are discussed fundamentals of selecting optimum parameters of the propulsion system on the whole.

During consideration of various types of liquid-propellant rocket engines in the book there are given fundamentals of theory of the operating process and designing, there are described specific character of operation of basic units and calculations of their characteristics, there are examined selection of ZhRD schematic diagram, combined operation of its units and method of calculations of optimum parameters.

The book is intended as a training aid for students of higher educational institutions, specializing in rocket engines; it can be of interest for engineers working in the field of rocket technology.

While compiling the book, we considered that students attended courses of thermodynamics, gas dynamics, hydraulics and heat transfer.

While writing the book the authors used domestic and foreign literature from the field of rocket engine manufacture.

Separate chapters of the book were written by: A. P. Vasil'yev and V. M. Polyayev — Chapters II, VI, VII, XVII; V. M. Kudryavtsev — Chapters III, IV, VIII, XVIII; V. A. Kuznetsov — Chapter XIV; V. D. Kurpatenkov — Chapters IX, X, XI, XII; A. M. Obel'nitskiy – Chapters XIII, XV, XVI, XIX; V. M. Polyayev – Chapter I; B. Ya. Poluyan – Chapter V; V. M. Kudryavtsev and V. D. Kurpatenkov together compiled Chapter XX.

Critics

1. F. L. Yakaytis, Prof.
2. L. S. Dushkin, Prof.

CHAPTER I

GENERAL INFORMATION ABOUT ROCKET ENGINES

§ 1. Terminology and Specific Peculiarities of Rocket Engines

For accelerated travel of some vehicle (rocket, aircraft, etc.) or for overcoming forces of external drag (aerohydrodynamic, gravitational forces), to this vehicle there should be applied force, called thrust.

Thrust is created by the propulsion system (engine), installed on the vehicle. Thrust is reactive force, appearing with rejection of some mass (working medium) from the engine, with this the direction of thrust and motion of rejected working medium are opposite.

The thrust magnitude, determined by equation of momentum, is proportional to the product of mass of working medium by its rejection velocity.

For creation of a specific rejection velocity of working medium, energy should be supplied to it. The greater the amount of energy that is supplied to a unit of mass of working medium, the higher is its rejection velocity and the greater the thrust developed by the engine.

Thus, for creation of thrust there is necessary the presence of working medium, energy source and installation — engine, converting energy into kinetic energy of working medium.

Depending on the type of engine, it can completely use energy and working medium from the environment or in another case energy source and working medium reserve are completely aboard the vehicle.

An intermediate position is occupied by various types of engines, which completely or partially use energy or working medium from the environment.

Engines obtaining energy or working medium or both together from the environment pertain to the class of nonrocket engines. For example, these include various types of jet engines (turbocompressor, ramjet, bypass), "Zond-2" type plasma electrojet engine, for which the supply of working medium is completely aboard the vehicle, but it obtains energy (solar) from the environment.

Thus, a rocket engine is an installation having energy source and a working medium supply, designed for production of thrust by conversion of any form of energy into kinetic energy of working medium, rejected from the engine into the environment.

From this definition of a rocket engine there stems its basic difference from other types of engines — autonomy from the environment.

It is necessary to point out that by autonomy of rocket engine it is impossible to mean independence of its parameters from the environment. Output parameters of a rocket engine considerably depend on ambient pressure (counterpressure). By autonomy one should understand only the ability of a rocket engine to operate without use of the environment.

At the contemporary level of technology in rocket engines there can be used energy, accumulated in form of nuclear, electrical, thermal and chemical.

Rocket engines, using nuclear, electrical and thermal energy, make up the class of nonchemical rocket engines (see Fig. I.1). These engines are as yet in the theoretical development and experimental investigation stage.

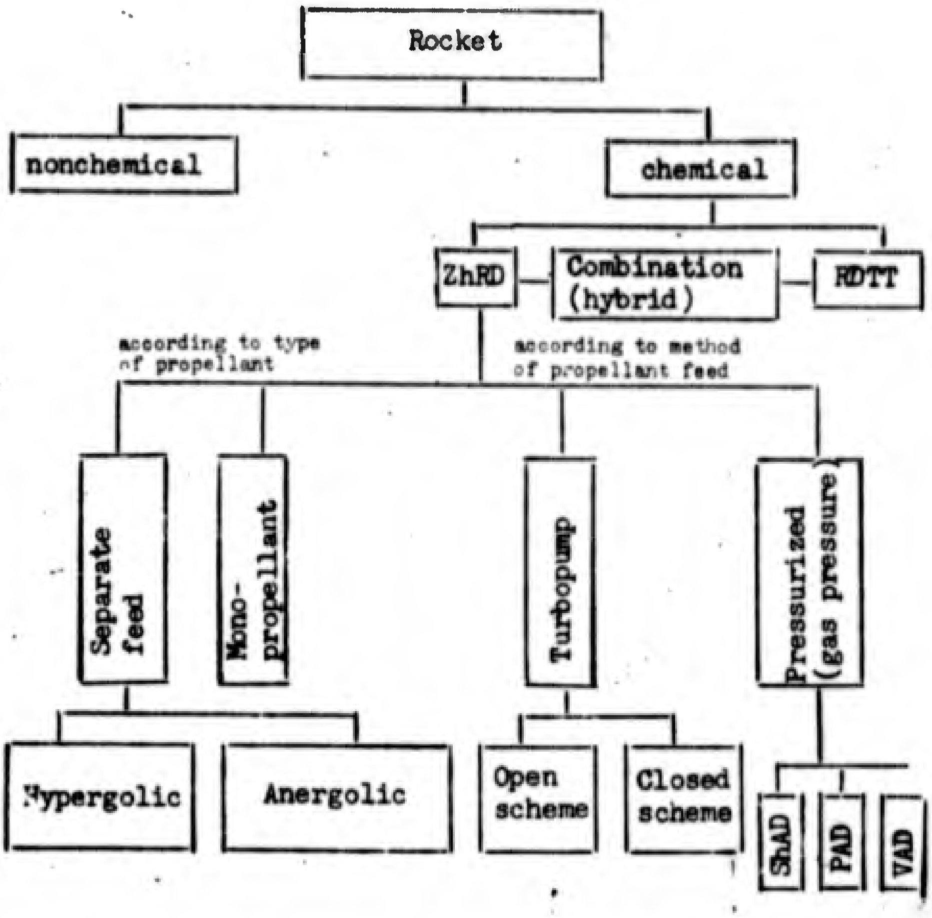

Fig. I.1. Classification of rocket engines.

The overwhelming majority of rocket engines practically applied at present use chemical energy – chemical propellant. The propellant can be mono-, bi- and multipropellant. At present in most engines there is used bipropellant, consisting of fuel and oxidizer. The energy source in this case is the reaction of burning (exothermic reaction, occurring with heat liberation).

Exothermic reaction can also be the reaction of decomposition of certain substances, or association (recombination) of radicals.

Chemical energy of propellant in the engine combustion chamber is converted into thermal energy of reaction products (combustion products). Then in the engine nozzle thermal energy will be converted into kinetic energy of outflowing combustion products, as a result of which reactive force (thrust) is formed.

Thus, initial chemical propellant is simultaneously both an energy source and a source for producing working medium. Totality of the noted criteria defines the class of chemical rocket engines. The most characteristic for these engines are thermal processes, therefore they belong to the thermal category.

Chemical rocket engines (Fig. I.1), depending on the state of matter of utilized propellant, may be divided into the following basic groups.

1. Engines using solid propellant (RDTT).

2. Engines using propellant with mixed state of matter — combination (hybrid) engines, for which one of the propellant components is in liquid, and the other is in solid phase.

3. Engines using liquid propellant (ZhRD).

In RDTT the solid propellant, being a physical or chemical mixture of oxidizer and fuel (propellant charge), is usually located inside the combustion chamber.

In hybrid engines the propellant components, being in solid phase, is placed inside the combustion chamber, and liquid is fed to combustion chamber from a tank by a special supply system (feed system).

In liquid-propellant rocket engines both propellant components are placed in separate tanks and are introduced into the combustion chamber also by a feed system.

Basic characteristic peculiarities of rocket engines as compared to other types of engines will be the following.

1. Autonomy, permitting operation without use of the environment (under water, in the atmosphere, in a vacuum).

2. Nondependence of thrust on speed of the vehicle (see Chapter III).

3. High energy contents of propellant, caused by the tendency to obtain the highest possible exit velocity, and, as a result of this, large calorific intensity of the operating process and small specific gravities (engine weight per unit of developed thrust).

Besides the enumerated criteria, for chemical rocket engines high specific fuel consumptions (fuel consumption per unit of developed thrust), caused by the necessity of having fuel and oxidizer aboard the vehicle, are characteristic criteria.

The shown peculiarities determine the field of application of rocket engines.

Of the entire variety of rocket engines we will limit ourselves to consideration only of the liquid-propellant rocket engine (ZhRD), which has received wide practical application and occupies a special place in rocket technology and, in particular, in conquering outer space.

§ 2. Fundamentals of a Liquid-Propellant Rocket Engine

Liquid-propellant rocket engine consists of tanks, fuel component supply system (feed system), combustion chamber and nozzle, starting, control and cutoff systems.

Fuel feed to combustion chamber can be carried out by pressurized feed system or by pumps. In the latter case the system is called turbopump (TNA), since for pump drive, as a rule, a turbine is used.

On Fig. I.2 there is shown a diagram of an engine with pressurized feed system. Principle of action of the system consists of the fact that to the fuel tank there is fed gas, creating definite pressure in it, under action of which the propellant components are fed to the combustion chamber. Source of gas can be cylinders

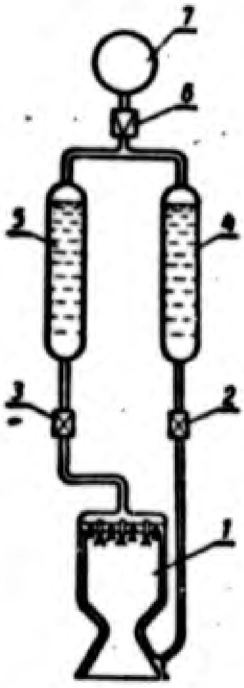

Fig. I.2. Diagram of liquid-propellant rocket engine with pressure feed system: 1 — combustion chamber; 2 — oxidizer cutoff valve; 3 — fuel cutoff valve; 4 — tank with oxidizer; 5 — tank with fuel; 6 — pressure regulator; 7 — VAD.

with air — air pressure accumulator (VAD); gas generator, operating on liquid propellant — liquid fuel pressure accumulator (ZhAD); gas generator with solid fuel charge — solid fuel pressure accumulator (PAD).

Advantage of the examined feed method of propellant components over the turbopump feed system consists of comparative constructive simplicity. But at the same time the application of a pressurized feed system leads to loading of tanks, inasmuch as in this case they are loaded by pressure from within, exceeding the pressure in combustion chamber. This narrows the field of application of pressurized feed system.

Figure I.3 shows a diagram of liquid-propellant rocket engine with turbopump feed system. For feeding each propellant component there is used its pump or a group of pumps. Rotation of pumps is accomplished by a gas turbine. Turbine is driven by gas, obtained in the gas generator, which produces gas (working medium of turbine) from parent substances, stored aboard the rocket beforehand. Exhaust from the turbine is either ejected into the atmosphere (open scheme) or enters the engine combustion chamber (closed scheme). Engine starting, control and cutoff systems consist of a series of units

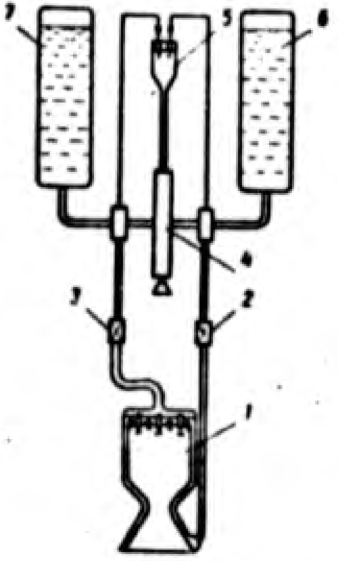

Fig. I.3. Open scheme of liquid-propellant rocket engine with turbopump feed system: 1 – combustion chamber; 2 – fuel cutoff valve; 3 – oxidizer cutoff valve; 4 – turbopump unit; 5 – ZhAD; 6 – tank with fuel; 7 – tank with oxidizer.

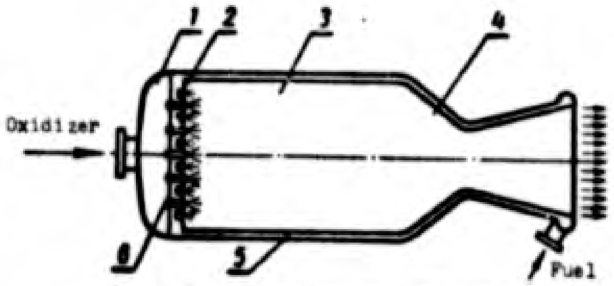

Diagram of liquid-propellant rocket engine combustion chamber

Fig. I.4. Diagram of combustion chamber of liquid-propellant rocket engine: 1 – head; 2 – fuel injector; 3 – combustion chamber; 4 – nozzle; 5 – cooling jacket; 6 – oxidizer injector.

(cocks, regulators, reducers, valves, etc.), whose purpose is to carry out specific operations in prescribed sequence.

Thrust is created in liquid-propellant rocket engine by its combustion chamber. Diagram of combustion chamber and nozzle of a liquid-propellant rocket engine, operating on bipropellant, is shown in Fig. I.4.

Fuel and oxidizer are injected under pressure into the combustion chamber through atomizing devices – head injectors of combustion chamber, are mixed, vaporized and ignited. After ignition of propellant its burning occurs. Propellant combustion in the chamber occurs at high pressures (in some cases up to 150-200 atm and higher) and temperatures (3000-4500°K). Further, the combustion products flow from the engine nozzle into the environment, while temperature and pressure of gas are decreased, and its velocity increases, passing through local speed of sound in the critical section. Nozzle exit velocity is 2700-4500 m/s. The higher the nozzle exit velocity of gas and its mass, the greater the thrust created by the chamber.

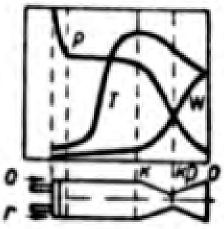

Fig. I.5. Change of pressure (p), temperature (T) and velocity (w) of combustion products along the length of liquid-propellant rocket engine chamber.

Approximate character of change of temperature, pressure, and velocity of gases along the length of engine combustion chamber and the nozzle is shown on Fig. I.5.

High thermo- and gas-dynamic parameters (pressure, temperature, velocity) of gas, and also the corrosion and erosion effect of gas flow on the chamber and nozzle walls, cause extremely arduous operating conditions of these elements.

For providing reliable operation of combustion chamber and nozzle there are used special methods for protection of walls. For example, intense external (circulated) cooling, creation of a parietal zone with lowered gas temperature (internal cooling), special wall coatings, etc. Usually external cooling is carried out immediately by either one propellant component or two. In cases when external cooling does not provide reliable operation of the chamber and nozzle, we use additional internal cooling, which loweres specific engine thrust.

§ 3. Basic Parameters Which Characterize the Liquid-Propellant Rocket Engine

Basic parameters which characterize liquid-propellant rocket engines include:

engine thrust — P, kgf. The thrust magnitude permits indicating propulsion system scales (its weight and overall dimensions). Existing liquid-propellant rocket engines have thrusts from fractions of grams to several hundreds and thousands of tons.

Thrust developed by the engine can be changed during its operation. Dependence of thrust change in time is called thrust-time curve. Thrust-time curve is calculated for a given type of aircraft depending upon its assignment and flight path;

specific thrust — $P_{уд}$, kg thrust/kg propellant/s. Thrust obtained from one kilogram of consumed propellant in one second is called specific thrust:

$$P_{уд} = \frac{P}{G_{сек}},$$

where $G_{сек}$ — propellant consumption per second, kg/s.

Specific thrust is one of the most important parameters, which permits indicating the engine quality, i.e., degree of perfection of the operating process, and energy efficiency of the propellant used. For contemporary liquid-propellant rocket engines $P_{уд}$ = 250-450 units.

Specific thrust primarily depends on type of propellant used and expansion ratio of combustion products in the nozzle. Specific thrust directly affects the flight range of the rocket. Thus, for an intercontinental missile with 11,000 km range and $P_{уд}$ = 310 kg thrust/kg-m/s the increase of $P_{уд}$ by one percent gives an approximately 500 km increase of range.

Development of liquid-propellant rocket engine tends toward increase of $P_{уд}$ by application of new energetic and more effective propellants, increase of expansion ratio of combustion products in the nozzle and improvement of the liquid-propellant rocket engine operating process.

Thrust and specific thrust depend on counterpressure of the environment. With decrease of counterpressure the thrust and specific thrust are increased and reach maximum value in a vacuum.

Total (complete) pulse – J_{Σ}. Total pulse is an integral of the function of thrust in time, taken over total operating time of the engine:

$$I_{\Sigma} = \int_0^{\tau_{\text{раб}}} P d\tau,$$

where $\tau_{\text{раб}}$ – overall operating time of propulsion system, s.

At constant engine thrust the total pulse is equal to the product of thrust by the duration of its operation:

$$I_{\Sigma} = P\tau_{\text{раб}} = P_{\text{уд}} G_{\text{т}},$$

where $G_{\text{т}}$ – weight of propellant in tanks, kg.

Total pulse is determined by the tactical and technical assignment of the aircraft and is one of the important parameters characterizing the engine.

Thus, for example, for liquid-propellant rocket engines we select some feed system or another depending on total pulse and the weight of the propulsion system.

Weight to thrust ratio – $g_{\text{дв}}$. By weight to thrust ratio we mean ratio of engine weight to its thrust:

$$g_{\text{дв}} = \frac{G_{\text{дв}}}{P},$$

where $G_{\text{дв}}$ – engine weight, kg.

Weight to thrust ratio characterizes the degree of weight perfection of the engine construction. For rockets this parameter is very important, since decrease of weight to thrust ratio leads to increase of flight range of the rocket. Therefore, the tendency to decrease of value of weight to thrust ratio is natural. For contemporary liquid-propellant rocket engines the weight to thrust ratio is already 0.015-0.01 and less.

Besides the enumerated basic parameters of liquid-propellant rocket engines, there should still be noted its operational, technical, and technological qualities, such as type of propellant used, starting multiplicity, one-time or repeated applicability, control range of thrust, reliability of its operation, service life, ease of servicing, etc.

All the above enumerated parameters permit judging liquid-propellant rocket engines on the whole and comparing them to each other, revealing advantages and disadvantages of some engine, and establishing rational fields of their application.

§ 4. Classification and Fields of Application of Liquid-Propellant Rocket Engines

In the basis of each classification lies the distinction of subjects with respect to some group of criteria. These criteria can be different. For example, assignment, design, operating process, peculiarities of feed system of working medium and engine control system, etc.

It is impossible to construct some universal classification of liquid-propellant rocket engines, since the quantity of such criteria and their groups is extremely great.

However, using design and operational considerations as a basis it is possible to separate basic distinctive peculiarities of rocket engines and on the basis of these construct the classification (see Fig. I.1, where as determining criteria there are used type of propellant and type of feed system). Regardless of this, it is also possible to classify liquid-propellant rocket engines by a number of other criteria, for example, by field of application.

Liquid-propellant rocket engines are used basically for three types of flight vehicles: rockets, spaceships and aircraft.

Depending on the field of application, liquid-propellant rockets are divided into the following basic classes.

1. Rockets designed for transferring payload from one point of the earth's surface to another. They are called "surface-to-surface" rockets. Here it is possible to relate rockets of analogous assignment, ship-launched, etc.

2. Rockets designed for delivery of a payload from the earth's surface to an orbital (space) trajectory — "surface-to-space."

3. Rockets designed for striking air targets. These rockets can be launched from the ground ("surface-to-air") or from aircraft ("air-to-air").

4. Rockets designed for striking targets located on the earth's surface or under water from the air ("air-to-ground," "air-to-water").

Liquid-propellant rocket engines are installed on aircraft either as the basic engine, or as a booster, providing short-term thrust augmentation. When a liquid-propellant rocket engine is the basic engine on the aircraft, such an aircraft carries the name rocket aircraft.

Let us consider conditions of application of liquid-propellant rocket engines on various types of flight vehicles.

"Ground-to-space" space rockets. To rockets of this type there are imposed requirements of delivery of a payload into a circumterrestrial orbit with orbital velocity (7.9 km/s) or higher velocities.

Usual space rockets consist of two, three and more rockets (stages), operating in series one after the other (Fig. I.6). First

Fig. I.6. Diagram of a three-step space rocket: 1 – first stage; 2 – second stage; 3 – third stage; 4 – payload.

the liquid-propellant rocket engine of the first stage is cut in. Payload for the first stage is the remaining stages. After burnout the first stage is separated and the following stage is cut in. After the second burnout the latter is separated and the engine of the following stage is cut in, etc.

Since the weight of the payload carried by each stage is successively decreased, then thrust developed by each stage is decreased accordingly. Thanks to this the fuel reserve, which is expended on acceleration of the payload to the predetermined velocity, is sharply reduced. The more stages the rocket has (at equal launch weights), the greater the payload that can be introduced into orbit.

However, increase of the number of stages complicates the operation and lowers the reliability of the rocket. Therefore, at present for increase of payload weight we use thrust augmentation of liquid-propellant rocket engines to values, measured in thousands of tons.

<u>Vernier liquid-propellant rocket engines of spaceships</u>. Vernier liquid-propellant rocket engines are designed for change and correction of spaceship trajectory during orbital and interorbital flights.

To engines of this type there is imposed an intricate complex of requirements, caused by conditions of their operation. These include: high degree of reliability, prolonged stay in launch readiness conditions, repeated starting, possibility of change of direction of thrust vector and several others. Absolute value of thrust of vernier liquid-propellant rocket engines, as a rule, is very small (from tenths of a gram to several kilograms).

To the category of vernier liquid-propellant rocket engines it is possible to relate acceleration and retrorockets, designed for increase or reduction of spaceship velocity. They differ from vernier liquid-propellant rocket engines by large values of thrust, measured in hundreds of kilograms and above.

Combat rockets. After termination of the second world war rocket weaponry found wide application in many armaments.

On combat rockets there is imposed a number of stringent operational requirements, caused by the specific character of their application. The most important of these requirements are prolonged storage in a state of complete launch (combat) readiness, possibility of transportation in a state as close as possible to combat readiness, and several other requirements.

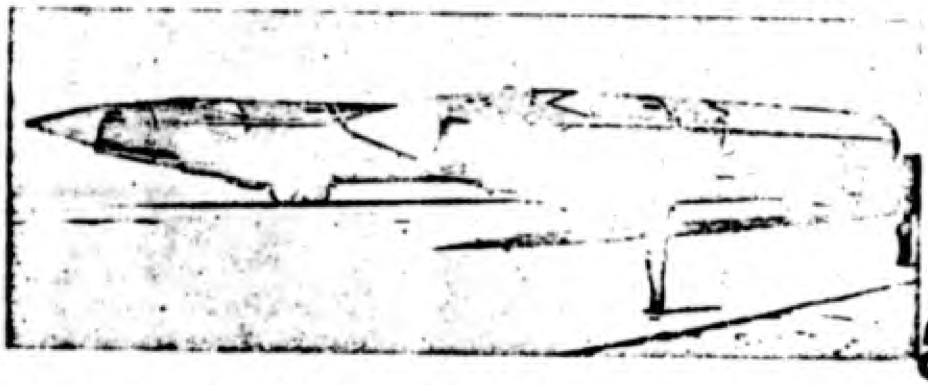

Fig. I.7. Multistage Soviet rocket on parade.

Let us consider some of the most important types of rocket weaponry.

Strategic rockets ("surface-to-surface").

Range of strategic rockets usually exceeds several thousand kilometers. For achievement of the prescribed range there can be used both orbital and ballistic trajectories. Engines of rockets of this type have value of developed thrust approaching the liquid-propellant rocket engines of space rockets.

On Fig. I.8 there is shown a Soviet strategic rocket.

Fig. I.8. Launch of Soviet strategic rocket.

Tactical rockets ("surface-to-surface," "water-to-surface," "water-to-water," "air-to-ground").

Tactical rockets differ from strategic by smaller range. As a result of this, the propulsion system of rockets of this class have smaller thrust and weight, and simpler construction. For example, launch and operation at raised counterpressure (for launch from under water), etc. Figures I.9 and I.10 show samples of a similar type of rocket.

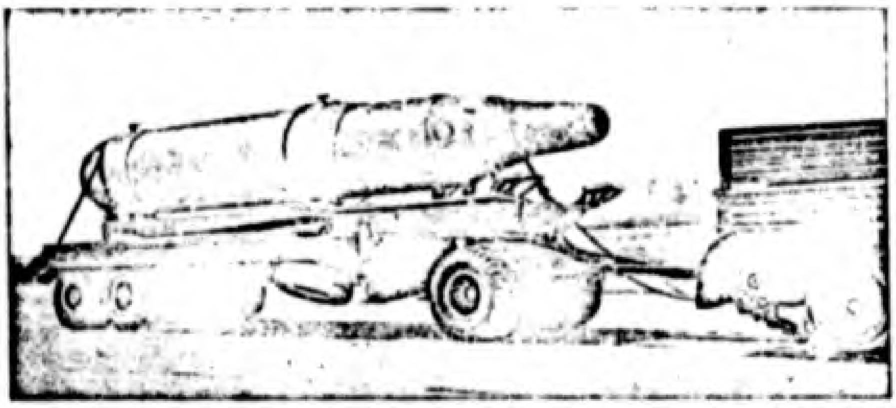

Fig. I.9. Soviet ballistic missile, submarine launched type, on parade.

Fig. I.10. Launch of Soviet rocket from a rocket carrying aircraft.

Surface-to-air guided missiles (ZUR) are of the "surface-to-air," "water-to-air" class. In connection with the appearance of high-altitude supersonic aircraft the surface-to-air guided missiles received wide application.

At the present time this class of rockets has attained a high degree of perfection. In the armament of contemporary armies there are found ZUR's with antiaircraft defense system complexes (PVO), possessing special detection and warning installations and capable with one shot (rocket) to knock down aircraft at practically any possible speed and altitude.

On the ZUR propulsion systems there are imposed especially

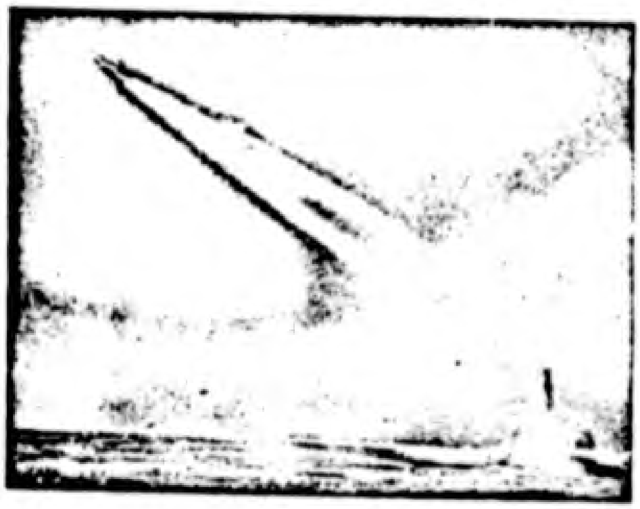

Fig. I.11. Launch of Soviet surface-to-air rocket from a ship.

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stringent requirements for maintaining constant launch readiness, minimum time of reaching launch conditions and low value of production and operation. Figure I.11 shows a similar type of ZUR.

In connection with the appearance of strategic and tactical rockets it became necessary to create means of intercepting and destroying them. In this case, as compared to a ZUR, the problem is complicated by the little time available for detection and interception of the object, and the necessity of its destruction at sufficiently large distance and high altitude from the defended zone.

For this there appeared a special class of rockets — antimissile missiles. In view of the specific conditions of operation, requirements of large launch thrust-to-weight ratio[1] and especially high reliability were imposed on them.

Rocket aircraft. Further development of piloted aviation will occur in the direction of mastering all high altitudes and flight speeds. In limiting case this will lead to the necessity of using liquid-propellant rocket engines as the basic engine for aircraft (rocket aircraft). Only a rocket aircraft is able to accomplish flights along orbital trajectories at suborbital speeds. Therefore, the future of stratospheric and high-speed aviation will apparently rest on the liquid-propellant rocket engine. Additional stimulus for the use of liquid-propellant rocket engines on similar piloted aircraft is the possibility of their multiple use, i.e., a rocket aircraft possesses practically the same merits as space or intercontinental rockets, while maintaining the economic advantages connected with multiple use.

At the present time the development of this area of technology is only started.

On liquid-propellant rocket engine designed for rocket aircraft there is imposed a number of requirements, determining its essential distinction from engines used for rockets. Primarily they include:

1) multiple launch and repeated use;

2) long service life with respect to operating time and number of launches;

3) wide thrust control range;

4) high degree of safety and reliability of operation.

At present there are experimental models of rocket aircraft in operation. One of them reached a flight altitude of over 100 km and flight speed over 6000 km/h.

Boosters. To assure flight vehicle takeoff there are used boosters with liquid-propellant rocket engines, use of which permits substantially reducing the length of takeoff run of an aircraft and provides takeoff with increased payload. On these engines there is imposed the requirement of repeated starting and reuse, and also minimum erosion and corrosion effect of combustion products, flowing from the engine nozzle, on construction of the aircraft and airstrip.

Other purposes. For example, liquid-propellant rocket engines are widely used for driving rocket sleds, moving along rails, for testing various rocket and aircraft components, connected with high speeds and considerable overloads.

It is possible to cite other examples of application of liquid-propellant rocket engines.

§ 5. Brief Review of Rocket Engine Development

Creation of the rocket engine pertains to the remote past. The earliest rocket engines known to us were the engines of solid-propellant rockets. They, as N. G. Chernyshov indicates (73), appeared simultaneously with the invention of gun powder.

From literature sources it is known that the first solid-propellant rockets appeared in China. In X-XIII centuries the application of gun powder and rockets was quite well known in Europe. Reliable data on the combat employment of rockets pertain to this time.

In Russia, as various historical sources show, the solid-propellant rocket appeared in the middle of the X century.

At the end of the XVIII century in Europe interest was awakened toward the military application of solid-propellant rockets first in England, and then in other European countries. Rocket forces appeared. Solid-propellant rockets were widely used in wars of the first half of the XIX century. Thus, for example, in the Crimean war period around 5000 combat rockets were produced annually in Russia. In the middle of the XIX century there appeared rifled guns, for which the range and sightability turned out to be the best as compared to the rocket weaponry, which led to rejection of the application of combat rockets. Gradually combat rockets were forgotten and the rocket forces abolished (rocket corps in Russia was abolished in 1897). However, the idea of the use of the jet propulsion principle continued to live and found its brilliant regeneration in the works of Konstantin Eduardovich Tsiolkovskiy (1857-1935), the founder of contemporary rocket technology.

In 1903 Tsiolkovskiy published an article "Investigation of Outer Space by Rocket Instruments," in the journal "Nauchnoye obozreniye" ("Scientific Review"), where for the first time he indicated a rocket with a liquid-propellant rocket engine as a means of movement in outer space, he outlined ways of mastery of interplanetary space and gave basic laws of rocket motion.

Tsiolkovskiy not only indicated theoretical bases of rocket flight, but he also gave the first schematic diagram of a vehicle with a liquid-propellant rocket engine, in which he provided all the basic equipment of contemporary engines of this type.

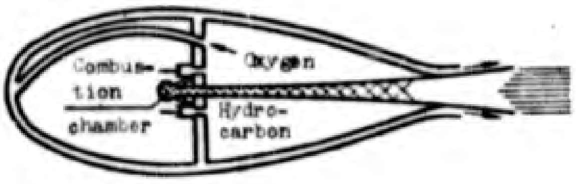

Fig. I.14. Diagram of K. E. Tsiolkovskiy rocket spaceship.

The first diagram of a flight vehicle, given by Tsiolkovskiy, is shown on Fig. I.14. As propellant he proposed using liquid hydrocarbons and oxygen. In 1903 and in subsequent years he investigated various propellants for liquid-propellant rocket engines, proposed using propellant components for cooling the engine, anticipated the necessity of forced feed of propellant components by pumps.

Tsiolkovskiy proposed several methods of rocket control, including vanes, placed in the gas outflow, and by turning the jet nozzle or the entire engine, installed on the rocket. Rocket control should be automatic during this.

As early as 1911 Tsiolkovskiy with great sagacity indicated the possibility of using atomic and electrical energy in rocket engines (11). He considered flight conditions of the rocket in interplanetary space, and conditions for departure of the rocket from earth. He proposed forming artificial satellites around the earth.

The idea of creating multistage rockets or, as he called them "rocket trains," making it possible to obtain considerably large terminal velocity as compared to a single-stage rocket, belongs to him.

From the above it follows that Tsiolkovskiy developed the project of space flight on a rocket with liquid-propellant rocket engine in almost all parts, laid the principle and theoretical foundations of contemporary rocket engine manufacture, thereby having determined for decades the forward path of development of jet apparatuses — rockets. Tsiolkovskiy's ideas did not receive acknowledgement in tsarist Russia, and only during Soviet rule was Tsiolkovskiy rendered aid in the work and publication of his labors.

In the twenties Tsiolkovskiy's ideas received world fame, his basic works were translated into foreign languages. In a number of foreign countries there were created groups and societies for the study of possibilities of interplanetary journeys, and there were developed design and experimental works on rockets and liquid-propellant rocket engines.

Practical realization of K. E. Tsiolkovskiy's ideas in the field of rocket technology, and also their further development was started by us only during the years of Soviet rule. With this the creation of liquid-propellant rocket engines paralleled the creation of rockets, and works in this area were closely connected.

In the thirties in the USSR there were created two organizations, setting the beginning of the development of a domestic school of rocket-building.

In 1929 to the development of electrical and liquid-propellant rocket engines there was devoted the first research and design organization in the staff of the gas-dynamic laboratory in Leningrad (GDL).

By the works of this organization there was theoretically and experimentally proven the possibility of creation and there was determined the field of expedient application of an electrical rocket engine, using metal as working medium and electricity as energy source. Here in 1930 oxidizers were proposed for liquid-propellant rocket engines for the first time: nitric acid, nitric tetroxide, hydrogen peroxide, perchloric acid, tetranitromethane and their solutions and colloidal fuel, containing beryllium. Such oxidizers as nitric acid and nitrogen tetroxide subsequently received the widest application in rocket technology.

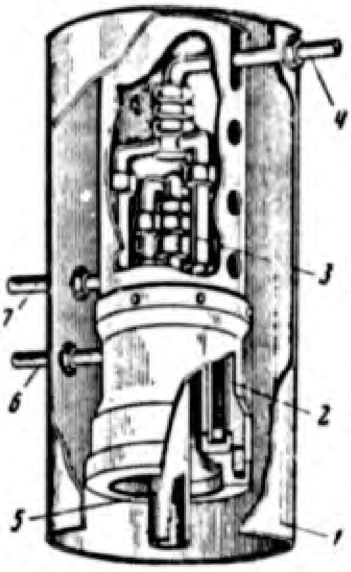

Fig. I.15. Soviet engine ORM-1: 1 – water jacket; 2 – combustion chamber; 3 – fuel feed to injector; 4 – oxidizer feed tube; 5 – nozzle; 6 – chamber pressure measuring tube; 7 – fuel feed tube.

In 1930-1931 passed the experimental rocket motor (ORM-1), developed in GDL, firing tests – one of the first liquid-propellant rocket engines. In 1931 about 50 bench tests were conducted with this liquid-propellant rocket engine. It operated on nitric tetroxide (nitrogen tetroxide) – as oxidizer and on toluene – as fuel. On Fig. I.15 there is shown the appearance and a cutaway of this engine. It consisted of a combustion chamber, covered inside with a thin copper sheet, cylindrical nozzle, oxidizer feed duct, and fuel feed duct. Ignition of propellant was carried out by ignition of wadding, inserted in the combustion chamber through a nozzle. At the same time there was proposed hypergolic propellant and a chemical source of ignition.

Another organization — jet engine section at Osoaviakhim [Society for Assistance to the Defense, Aviation and Chemical Construction of the USSR] under the direction of F. A. Tsander — was created in 1929 in Moscow. In 1931 it was converted to the Group for the Study of Jet Propulsion (GIRD). The great merit of GIRD colleagues involved the fact that they transferred the rocket problem from the area of theoretical research to the area of engineering practice. They first evaluated K. E. Tsiolkovskiy's ideas from practical positions and showed engineering methods for solution of problems on conquering space. In a short time they succeeded in developing several engines, installed them on rockets and launched them.

F. A. Tsander (1887-1933) actively participated in the publication of K. E. Tsiolkovskiy's works and the spread of his ideas, and in 1924 published his book "Perelety na drugiye planety"[2] ("Flights to Other Planets"). F. A. Tsander developed thermal calculations of the operating process of liquid-propellant rocket engines (i.e., calculation of combustion and outflow taking dissociation into account), and also the method of evaluating the economy of liquid-propellant rocket engines, on the basis of which he proposed new cycles of increased economy. He also proposed a method of calculating the temperature of chamber working wall of liquid-propellant rocket engines and a method for its cooling. To Tsander belongs the idea of using metallic constructions of the rocket, fuel and oxidizer tanks, pipelines, etc, as engine propellant after their need elapses. Thanks to combustion of these metallic parts the engine operating time is increased and weight characteristic is improved, which leads to increase of flight terminal velocity of the rocket vehicle. Even before organization of GIRD in 1930 F. A. Tsander successfully tested the OR-1 liquid-propellant rocket engine (Fig. I.16), initially operating on gasoline and air. Later, on this engine there was tested metal-containing fuel. The engine developed up to 5 kg thrust. The engine combustion chamber was cooled by air, which was subsequently used for burning of gasoline in the combustion chamber itself. In the engine there were provided replaceable nozzles, which permitted conducting different experiments. Numerous test firings were conducted on the OR-1 engine.

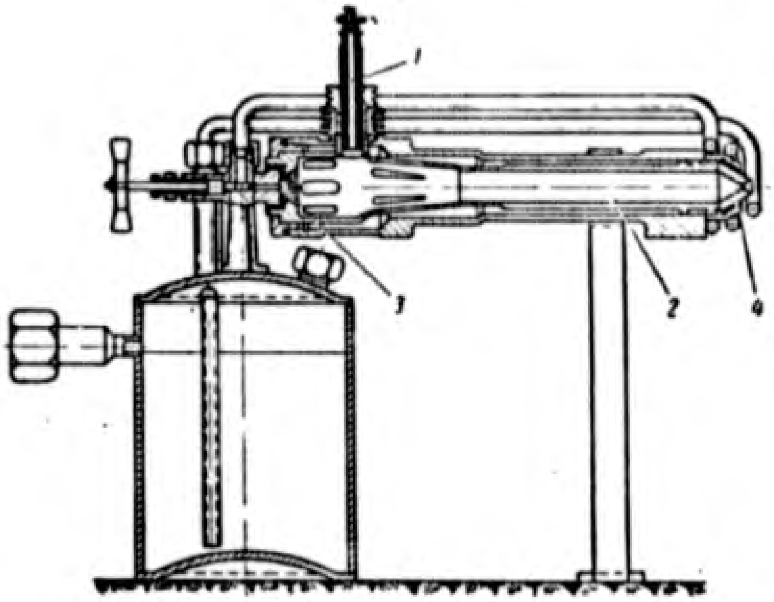

Fig. I.16. Diagram of OR-1 engine of F. A. Tsander's design: 1 — spark plug; 2 — combustion chamber; 3 — fuel injector; 4 — nozzle.

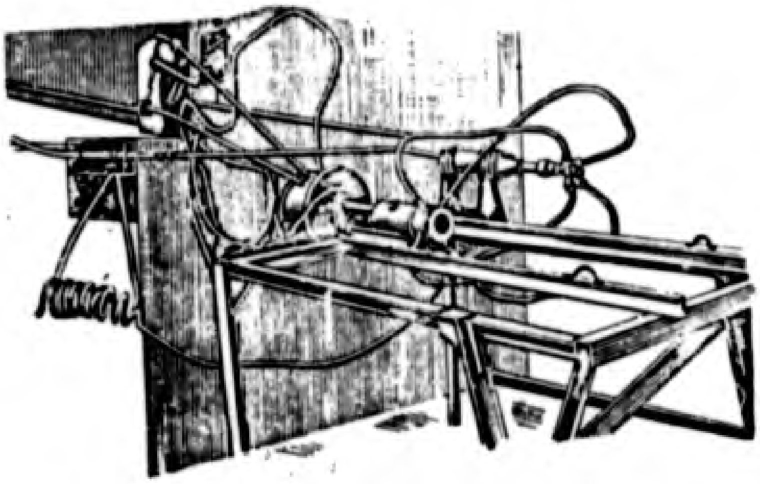

Fig. I.17. OR-2 engine of F. A. Tsander's design on the testing stand.

On the basis of obtained experience and theoretical developments there was proposed a program, extensive for that time, of works on creation of rocket engines, and the first step in its realization was the creation of liquid-propellant rocket engine OR-2 (Fig. I.17) with 50 kg thrust, operating on gasoline and liquid oxygen. This engine was tested in 1933 even after the death of F. A. Tsander. Feeding of combustible and liquid oxygen to the engine chamber was carried out by their displacement from tanks by gaseous nitrogen, which was produced by vaporization of liquid nitrogen by heating the tank. Oxygen, entering the engine, was preliminarily vaporized in two vaporizers and then directed to a jacket for cooling the combustion chamber. From the cooling jacket through slits in the combustion chamber walls it was introduced into the chamber, fuel was atomized by injectors located in the engine head. In the OR-2 engine a cryogenic (low-boiling) oxidizer – liquid oxygen, was used for the first time in the world.

In 1933 on the basis of GDL and GIRD in Moscow there was created the Rocket Scientific Research Institute (RNII), which as a basis for its works used the problem of development of theory and design of flight vehicles using the jet principle for their motion. The institute united enthusiasts working in the field of rocket-building, and contributed to a further stage of development of domestic rocket technology.

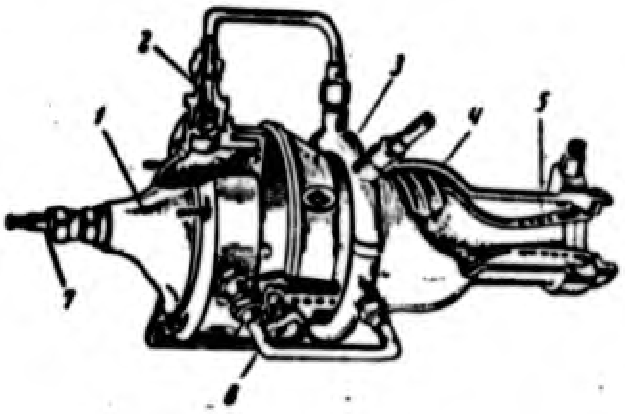

Fig. I.18. Soviet engine ORM-65: 1 – head; 2 – fuel feed tube; 3 – fuel manifold; 4 – rib-cooled combustion chamber; 5 – rib-cooled nozzle; 6 – oxidizer swirl injector; 7 – electric spark plug for ignition of explosive charge.

After creation of RNII the active members of the gas-dynamic laboratory group continued the development of liquid-propellant rocket engines. In 1936 there was created the ORM-65 engine (Fig. I.18), operating on nitric acid and kerosene. The engine developed up to 175 kg thrust, had specific thrust of 210 units and withstood repeated launching, which should be considered a good result for that time. The engine was installed on the 212 winged rocket (Fig. I.19) of S. P. Korolev's design. This rocket had a gross weight of 210 kg, and payload weight 30 kg. Design flight range was calculated at 50 km. Engine was installed on a frame in the tail

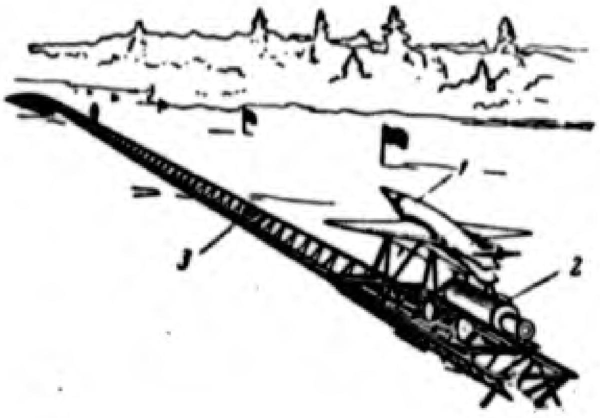

Fig. I.19. Soviet 212 winged rocket: 1 — winged rocket on catapult trolley; 2 — trolley booster; 3 — catapult rail.

section and was enclosed by a metal visor for protecting the rocket control vanes from fire. Feed of propellant components to the engine was pressurized. There were conducted ground and flight tests of the engine, which gave positive results. During the Patriotic War liquid-propellant rocket engines began to be installed on aircraft for takeoff boost and increase of their maneuverability. Thus, liquid-propellant jet engines RD-1, RD-1Kh3, RD-2 and RD-3, developed by this group, were installed on Pe-2, Lk-3, La-7, Su-7 aircraft and others. Lk-3 aircraft with the RD-1Kh3 engine (Fig. I.20) passed flight tests in 1945, showing a speed increase of 182 km/h at an altitude of 7800 m.

Fig. I.20. RD-1Kh3 engine installed on Lk-3 aircraft with cowling removed from engine.

Fig. I.21. "GIRD-Kh" rocket.

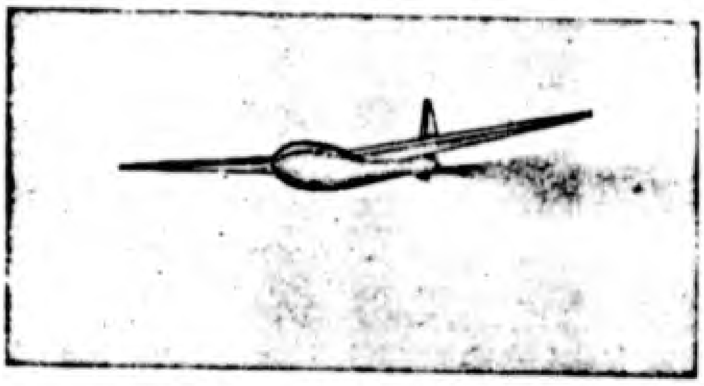

Fig. I.22. Soviet rocket aircraft in flight.

Another group, coming from the GIRD, worked on further improvement of the engines, using liquid oxygen as oxidizer. The group created a liquid-propellant rocket engine, which successfully passed bench tests in October of 1933. The engine operated on ethyl alcohol and liquid oxygen. There was obtained 75 kg thrust for 21 s.

In November of 1933 a GIRD-Kh rocket (Fig. I.21) with the shown engine successfully passed flight tests.

Subsequently the group created the 12-k engine with 306 kg thrust, operating on alcohol and oxygen and having an uncooled ceramic nozzle, and the RDA-1-150 engine, operating on nitric acid and kerosene. In particular, a rocket aircraft (Fig. I.22) of S. P. Korolev's design with the RDA-1-150 engine successfully accomplished the first flight 11 February 1939 piloted by F. A. Fedorov.

Subsequently a liquid-propellant rocket engine was installed on a rocket aircraft of V. F. Bolkhovitinov's design. The first successful flight of this aircraft was in 15 May 1942 piloted by

G. Ya. Bakhchivandzhi. This was the first rocket fighter airplane in the world.

Another group of colleagues of the GIRD, directed by M. K. Tikhonpavov, developed the original jet engine, which launched one of the first GIRD-09 rockets in August of 1933. This engine belonged to the category of combination (hybrid) engines operating on solid propellant and liquid oxidizer. The engine operated on solid gasoline (solution of rosin in gasoline) and liquid oxygen. Solid gasoline was located directly in the combustion chamber. Vaporization of oxygen was attained by its heating by propellant combustion products, and at the moment of engine starting – by combustion of a special explosive charge, which served for ignition of propellant in the chamber.

M. K. Tikhonravov's rockets with liquid-propellant rocket engines accomplished a number of successful flights in 1934, and in 1935 one of them reached an altitude of several kilometers.

Thus, the above mentioned brief review of the works of Soviet scientists in the area of rocket technology attests to wide span of research in the creation and practical use of liquid-propellant rocket engines.

Along with the above-indicated works of domestic scientists, in the second decade of the XX century the first research in theoretical questions of space flight appeared abroad, then both liquid and solid-propellant rockets.

Among the western scientists, dedicating their work to the shown problems, one should name R. Esnault-Pelterie (France), whose first works appeared in print in 1913, and R. Goddard (United States), starting his works in 1915 and later creating several types of liquid-propellant meteorological rockets, and also Germans H. Oberth and E. Sänger (Austria), who made great contributions to the theory of rocket flight.

The creation of liquid-propellant guided rockets (V-2) by the Germans during WW II appeared significant for their time.

In postwar years in the Soviet Union there was mastered an entire series of models of combat ballistic missiles, and also meteorological, and geophysical liquid-propellant rockets, with the aid of which there was conducted an extensive program of upper-atmosphere research.

Nineteen hundred and fifty-seven entered the history of mankind as the year of the successful launching of an artificial earth satellite. After the first satellite followed no less magnificant achievements, such as the launching of heavy artificial earth and sun satellites, circling the moon and photographing its dark surface and, finally, putting artificial earth satellites with animals into orbit and their safe landing.

All these successes permitted the Soviet Union for the first time in the history of man to carry out manned space flight. On 12 April 1961 Major Yu. A. Gagarin rose into space aboard the spaceship "Vostok," accomplished flight around earth and safely returned.

On 6 August 1961 there was carried out a new launching of the spaceship "Vostok-2" with cosmonaut G. S. Titov, who accomplished 17 orbits around the earth.

In August 1962 for the first time in the world there was accomplished a formation flight of two spaceships "Vostok-3" and "Vostok-4," piloted by pilots-cosmonauts A. G. Nikolayev and P. R. Popovich.

In June 1963 there was made another formation flight on ships "Vostok-5" and "Vostok-6" with board pilots-cosmonauts V. F. Bykovskiy and V. V. Tereshkova-Kikolayeva aboard, where for the first time in the world the spaceship was controlled by a woman.

On 12 October 1964 for the first time in the world the three-seated piloted craft "Voskhod-1" was placed in orbit; aboard the craft was a crew consisting of pilot-cosmonaut V. M. Komarov, craft commander, scientific colleague-cosmonaut K. P. Feoktistov, and physician-cosmonaut B. B. Yegorov.

In March 1965 there was accomplished a successful flight of the spaceship "Voskhod-2" with pilots-cosmonauts P. I. Belyayev and A. A. Leonov. During this flight for the first time in the world there was accomplished the egress of a man from the spaceship into space.

Successful spaceship flights give the possibility of deeply investigating a number of new geophysical problems and studying the problem of manned flight in space.

In February 1966 there was carried out a soft landing of the Soviet automatic station "Luna-9" on the surface of the moon, after two months the Soviet automatic station "Luna-10" was placed into a circumlunar orbit – creating the first artificial moon satellite in the world. These flights were the first steps in the practical mastering of other planets of the solar system.

In a comparatively short period of development the contemporary liquid-propellant rocket engines reached large perfection. Propulsion systems are created for aircraft of various assignment. Engines are made which satisfy the most various operational requirements with different fuel feed systems, sharply differing both with respect to schematic diagrams and in terms of structural elements. There are developed engines which operate on various propellant components, both high-boiling and low-boiling (cryogenic).

At present liquid-propellant rocket engines continue to be developed and improved in the direction of increase of specific thrust, decrease of specific gravity and dimensions, increase of their reliability both in conditions of circumterrestrial and in the space zone of operation of rocket vehicles of the most diverse assignment.

Footnotes

[1] The ratio of thrust developed by the engine to the launch weight of the rocket is called the thrust-to-weight ratio.

[2] F. A. Tsander. [Problem of Flight by Rocket Vehicles]. Oborongiz, 1947.

CHAPTER II

THERMODYNAMIC AND GAS-DYNAMIC FUNDAMENTALS OF THE WORKING PROCESS IN THE COMBUSTION CHAMBER

Basic output parameter of a liquid-propellant rocket engine is reactive force of the working medium flowing from the nozzle box. Usually at the nozzle box exit the working medium is in gaseous state and the reactive force of the outflowing gas jet is basically determined by the mass flow rate per second of the working medium and the exit velocity, reached at nozzle exit.

At the prescribed flow rate per second of the working medium the reactive force will be greater, the higher the value of exit velocity of working medium from the nozzle box that is attained.

In basic types of existing liquid-propellant rocket engines the chemical energy of propellant is first converted into thermal, and then into kinetic energy of the outflowing gas jet. Therefore, the attainable value of exhaust velocity (besides the degree of perfection of the propulsion system) is determined by propellant chemical energy reserve and its thermodynamic properties, and also by conditions of conversion of one form of energy into another.

Usually the energy conversion conditions are determined by the design configuration of the propulsion system of liquid-propellant rocket engines and prescribed pressure limits, in which thermodynamic processes are carried out.

The purpose of thermodynamic and gas-dynamic analysis is determining optimum conditions of energy conversion and calculating the change of working medium parameters along the propulsion system ducts. Such a problem is very complex, since as the working medium it is necessary to be concerned not with individual substances in the form of chemically inert liquids or gases of constant composition, but with combustion products, in which during motion along the ducts of combustion chamber and nozzle box at high temperature there continuously occur various chemical reactions, changing the composition and properties of these real working mediums. Therefore, in addition to the determination of usual thermodynamic parameters p, T, v and flow rate w there appears the problem of finding composition and thermodynamic properties of reacting combustion products.

Theoretical analysis of phenomena is complicated by the fact that motion of working media occurs at high velocities, reaching sound propagation velocity and supersonic speed, at which the time the reaction products stay in combustion chamber and in nozzle boxes becomes very small, measured in thousandths of a second. For this reason we are not able to establish equilibrium states between thermodynamic parameters and the properties of working media.

In most cases, when perceptible disturbances of equilibrium appear (especially in chemical reactions), the degree of this nonequilibrium is indeterminate, not yielding to preliminary theoretical evaluation.

Therefore, the basic theoretical scheme for thermodynamic calculations provides the assumption that all processes are equilibrium. Such a method in application respect is accessible for conducting analyses, and by it there are performed most engineering calculations.

In cases when assumptions on possible nonequilibrium are especially weighty, there are conducted additional thermodynamic calculations with allowances for extreme limiting cases of complete absence of equilibrium with respect to all or separate parameters.

A comparison of the results of these two limiting calculation schemes can be evaluated in terms of how strongly one or another form of nonequilibrium may have an influence, and the comparison of computed values of parameters with data of engine tests gives the possibility of selecting the final method for calculations.

In spite of the complexity of phenomena, in liquid-propellant rocket engine theory there is developed a method for carrying out thermodynamic and gas-dynamic calculations, available for engineering practice, in which there are used calculation formulas initially obtained for idealized nonreactive working media. Such formulas can easily be derived by known thermodynamic and gas dynamic methods.

In basic regularities, utilized by thermodynamics and gas dynamics (equations of state of working medium, equations of conservation of energy, inseparability and force pulse), properties of various gases are considered by a small quantity of physical quantites, which include molecular weight μ, gas constant R_μ, heat capacities c_p, c_v, heat capacity ratio $k = c_p/c_v$ and sound propagation velocity a.

For ideal media of the same chemical composition these physical quantites are taken as constant and during integration of fundamental equations are carried as integral sign.

As applied to real reacting working media with variable physical properties and variable chemical composition, such a method of integration of fundamental equations will turn out to be approximate. This is a methodical assumption, which is justified by accessibility of conclusions and simplicity of obtained analytic dependences, making it easy to use them in the applied purposes.

Loss of calculation accuracy with such a method of integration is inevitable, however it is compensated to a considerable degree by the fact that in obtained final calculation equations it again turns out to be possible to introduce into consideration the variable values of physical properties, reflecting the behavior of real working media and combustion products of variable composition. Introduction of variable (or average) values of physical properties of the real working media into final calculation formulas permits bringing the calculation accuracy to the level of requirements of engineering problems.

With the shown assumptions in this chapter there are examined analytic relationships between thermodynamic and gas-dynamic parameters of gaseous working media. In these relationships the working media are characterized only by their physical properties: μ, R_{μ}, c_v, c_p, k, and a.

Determination of the enumerated physical properties for reacting combustion products of variable chemical composition is performed on the basis of thermochemical calculations by the method discussed in Chapters VI and VII.

§ 1. Working Media in a Liquid-Propellant Rocket Engine as Thermodynamic System

Usually in propulsion system ducts there occurs motion of either liquid or gaseous homogeneous working media. Only for combustion chambers and in nozzle boxes it is necessary to encounter heterogeneous combustion products, being polyphase mixtures (gaseous, liquid and solid components).

Physical structure of gas and liquid is discrete, the gas and liquid consist of molecules and atoms, which accomplish chaotic thermal motions inside the moving flow mass. Displacements of atoms and molecules from collision to another collision are determined by the value of the mean path of molecules, which depends on gas density.

In conditions of ducts, along which there occurs motion of working media in propulsion systems of liquid-propellant rocket engines, the density is so much greater that the gaseous working media can be considered as continuous media. To these media are attributed the following properties: inside molar volumes of gas there occur chaotic motion and collision of atoms and molecules, during chaotic thermal motion the separate particles can abandon the examined volume and be replaced by others, so that the overall mass of particles in this volume is not changed and such replacement of atoms and molecules inside the volume affects neither the average chemical composition of particles nor the velocity distribution of thermal motion.

Methods of phenomenological thermodynamics, used in liquid-propellant rocket engine theory, permit being diverted from discrete structure of working medium, permit not considering the internal molecular structure and permit operating by macrophysical properties (such as pressure, temperature and so forth), characterizing the total effects.

This is permissible if the studied volumes of substance are sufficiently great as compared to the dimensions of elementary particles and the distances between them, i.e., when it may be assumed that in the considered volume there is so many particles that distribution of their individual parameters of state conforms to random functions of mass distribution (Maxwellian distribution for velocities of molecules and others).

The presence of essential deviations from such distribution functions in gaseous working medium can be assumed at the nozzle box exit at very low gas density and with nonequilibrium processes.

In such cases for description of the behavior of working medium it would be necessary to resort to methods of statistical thermodynamics, operating by ideals of microphysical nature (number and structure of various atoms, molecules and other particles, their mass and energy and so forth).

For the majority of calculations in liquid-propellant rocket engines it is necessary to be concerned with equilibrium processes at rather high gas density, therefore all basic theoretical relationships between parameters in the liquid-propellant rocket engine are derived on the basis of phenomenological thermodynamics, with description of the working medium as a continuous medium.

Static thermodynamic methods are used only during theoretical calculations of tabular values of physical and thermodynamic properties of working media, such as heat capacity (at high temperature), internal energy, chemical equilibrium constants and so forth. It is necessary to resort to them in exceptional cases, in the absence of needed tabular data.

During the study of the behavior of working medium in propulsion system ducts of liquid-propellant rocket engine it is considered as a thermodynamic system, limited by control surfaces. Most often as control surfaces there are considered the solid channel walls, along which motion of working medium occurs.

For study there are selected certain molar volumes of gas, corresponding to one kilogram, one mole of working medium or any other quantity N_x, playing the role of a scale, at which it is permissible to consider the selected volume as a continuous medium.

Inside the studied volume the properties and parameters of working medium are considered identical at all points. Subsequently, regularities for selected volume are extended to regularities of any mass of working medium, participating in processes of energy conversion in liquid-propellant rocket engines.

Two forms of motion are inherent to this volume of working medium under conditions encountered in liquid-propellant rocket engines:

1) displacement along propulsion system ducts as a solid body (mechanical motion);

2) internal processes of transformation in the thermodynamic system itself (inside the considered volume).

Displacement along propulsion system ducts can occur under action of external forces (external influences), due to energy supplied to the examined system from outside, or under action of internal processes (due to expansion and other internal effects), due to internal energy.

In fuel feed lines, in combustion chambers and in nozzle boxes the flow is considered as one-dimensional mechanical forward flow.

In blade units there occurs mechanical rotation.

Internal processes of transformations of working medium in liquid-propellant rocket engine conditions can be connected with change of forces of surface tension (atomization of liquid-propellant), with phase transformations (fusion, vaporization or condensation), with diffusion phenomena with thermal phenomena, with expansion or compression of gaseous working medium (compressibility of propellant in liquid state is disregarded), with chemical reactions and change of mass of separate reactants (composition of combustion products), and with phenomena of perceptible thermal ionization (at combustion temperature over 5000°K).

The possibility of development of any form of displacements or internal motions of the material is called corresponding degree of freedom.

The presence of a considerable number of degrees of freedom, especially in conditions of combustion chambers and nozzle boxes of liquid-propellant rocket engines, leads to the necessity of considering general equations, characterizing the behavior of working medium with mutual transformations of various forms of motion.

Manifestation of each concrete form of motion is always connected with change of corresponding physical parameter X_i, called coordinate: displacement (with mechanical forward motion), angle of rotation ϕ (during rotation), momentum $k = mw$ (with kinetic displacement of system), moment of momentum M_K (with kinetic phenomena of rotation), height h (with displacement under action of gravitational forces), volume v (during expansion or compression of gas), entropy s (with thermal motion), mass of reactants M (during phase transitions and chemical reactions), surface f (with atomization of liquid into drops), electrical charge q (if electrical interactions are assumed).

and so forth.

Invariablity or the absence of corresponding form of motion are determined by constancy of the shown physical parameters (coordinates) $X_1 = \text{const}$.

In a thermodynamically isolated system there is established equilibrium between various types of motions and change of these parameters is ceased. Thus, equilibrium states of the system are characterized by certain constant values of the shown parameters, which it is possible to call parameters of state.

Appearance and development of each concrete form of motion is determined by the presence of corresponding propulsive force P_1 (potential): force (with mechanical forward motion), moment of force M_p (during rotation of system), velocity w (with kinetic forward motion), angular velocity ω (during kinetic rotation of system), force of inertia y (with unsteady forward motion), moment of inertia force M_y (with unsteady rotation), weight of body G (with gravitational phenomena), surface tension σ (with atomization of liquid), pressure p (with expansion or compression of gas), chemical potential κ (during phase transitions and chemical reactions), and absolute temperature T (with thermal phenomena).

Thus, for each form of motion the presence of two conjugate values is characteristic: propulsive force (potential) P_1 and physical parameter (coordinate) X_1.

If the system is limited by only one degree of freedom, then between these two conjugate values there exists functional connection

$$P_i = f_i(X_i), \qquad \text{(II.1)}$$

which is called equation of state.

The form of function $P_1 = f_1(X_1)$ is determined by properties of the system. By this equation P_1 is simply connected to X_1. In order to determine the state of a system with one degree of freedom, it is sufficient to assign either the value of P_1 or the value of X_1.

Consequently, in this case potentials may also be called parameters of state, as coordinate X_1.

All forms of motion are connected with conversions or transmission (exchange) of energy. Therefore, energy is a general single measure for evaluating all forms of motion of matter.

As a quantitative measure for evaluating all forms of motion without exception and interactions corresponding to them there is used the idea of generalized work, determined by equation

$$dL_i = P_i dX_i. \qquad (II.2)$$

Concrete types of work have names corresponding to forms of motion: mechanical work, kinetic work (force of impact or kinetic energy), thermal work (heat or thermal energy), chemical work (chemical energy), electrical work (electrical energy) and others.

Behavior of working medium in concrete unit form of motion (at one degree of freedom) can be fully determined by equation of state of type (II.1) and by quantitative degree of motion, determined by equation (II.2). It is convenient to study various types of motion in corresponding conjugate coordinates of type P_1-X_1, as is shown in Fig. II.1, where parameters of state and value of work $L_1 = \int P_i dX_i$ during transition from state 1 to state 2 are easily presented graphically.

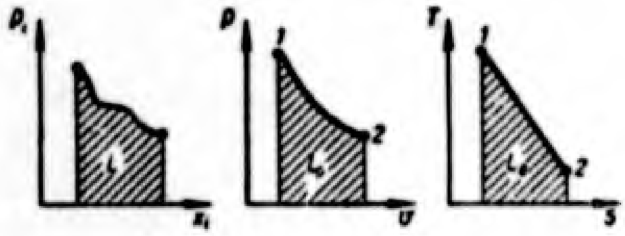

Fig. II.1. Representation of motion (process) in conjugate coordinates: L – generalized work, L_p – work of gas expansion; L_Q – thermal work (heat participating in the process).

In liquid-propellant rocket engine conditions the studied system usually has several degrees of freedom for various types of motion. In this case finding the connections between potentials P_1 and parameters X_1 is complicated because the different types of motion turn out to be interconnected.

Generally for i degree of freedom of internally connected forms of motion, instead of equation (II.1) the system of equations of state will be written so:

$$\left.\begin{aligned} P_1 &= f_1(X_1, X_2 \ldots X_i); \\ P_2 &= f_2(X_1, X_2 \ldots X_i); \\ &\cdots\cdots\cdots\cdots \\ P_i &= f_i(X_1, X_2 \ldots X_i). \end{aligned}\right\} \qquad (II.3)$$

For each degree of freedom the quantitative measure of corresponding form of motion will be generalized work according to equation (II.2), and quantitative appraisal of mutual transitions of one form of motion into another is established in accordance with law of conservation of energy:

for isolated system

$$dU = 0; \qquad (II.4)$$

with external influences

$$dU = \sum_1^i dL_i, \qquad (II.5)$$

where dU – change of internal energy of system; $\sum_1^i dL_i$ – sum of works of external influences with respect to all possible degrees of freedom.

Equations of state (II.3) and equation of conservation of energy reflect the basic property of the matter, appearing in interconnection of the most diverse forms of motion of matter.

The difference between these two types of fundamental equations consists of the fact that equations of state are connected with the mechanism of internal interconnection of various phenomena, but equation of conservation of energy touches only the quantitative side of energy transformation.

Detailed explanation of the mechanism of internal interconnection for many possible degrees of freedom, i.e., determination of equations of state in general form, as they are written in system (II.3), is not possible. Some equations of state are known for three degrees of freedom, but they are very complex and are not used.

For application purposes the equations of state must be simplified, i.e., in the basis of study there must be placed simplified concepts of the mechanism of interconnection of various phenomena. Such simplifications are based on the fact that certain internal connections between various phenomena are very perceptible and others are less noticeable, and in certain conditions it is possible to disregard them.

As an example let us consider the motion of ideal gas at three degrees of freedom: for gas expansion, for thermal motion of molecules and for forward kinetic motion of gas as a continuous medium. Designations of potentials, coordinates and generalized works for this case are listed in the following table:

Type of motion	Potential (propulsive force)	Coordinate (physical parameter)	Generalized work
Gas expansion	Pressure $P_1 = p$	Specific volume $X_1 = v$	Work of expansion $dL_1 = pdv$
Thermal motion	Temperature $P_2 = T$	Entropy $X_2 = S$	Thermal influence $dL_2 = dQ = Tds$
Forward kinetic motion as continuous medium	Velocity $P_3 = w$	Momentum $X_3 = k = mw$	Kinetic energy $dL_3 = wdk =$ $= wd(mw) =$ $= d(mw^2/2)$

The system of equations of state (II.3) in this case should have been written in general form so:

$$P_1 = p = f_1(v; S; k);$$
$$P_2 = T = f_2(v; S; k);$$
$$P_3 = w = f_3(v; S; k).$$

For simplification of equations of state it is assumed that the mechanism of thermal motion of atoms and molecules does not depend on whether all the gas mass moves as a continuous medium or it is not displaced, i.e., one degree of freedom of kinetic motion is considered not connected with mechanisms of thermal motion and gas expansion. Then the simplified system of equations of state (II.3) will look so:

$$P = f_1(v; S);$$
$$T = f_2(v; S);$$
$$w = f_3(k).$$

In the first two equations of this system there is reflected the connection of only two degrees of freedom for thermal motion and gas expansion, and the third equation corresponds to one unconnected degree of freedom of the kinetic motion of gas mass as a whole body.

By exclusion of variables the first two equations can be reduced to one. More often from the number of variables in equation of state we exclude entropy, which is impossible to measure directly by instruments, then we obtain equation

$$p = f(v; T),$$

which for gas is sufficiently studied and accessible for practical usage.

Simplified equations of state introduce some error into calculations, however the overall results of calculations can be satisfactory with practical accuracy, since the quantitative appraisal of transitions of one form of motion into another is principally based on the application of equations of conservation of energy, which do not depend on concepts of mechanism of motion. Similar simplifications of equations of state are made in examining the interconnection between other phenomena. In particular, it is considered that chemical phenomena do not affect the mechanism of thermal motion of particles, making up the gaseous working medium, gravitational forces also do not affect thermal motion and so forth.

In liquid-propellant rocket engine theory the most complex calculations are thermodynamic and gas-dynamic during motion of combustion products which are mechanical mixtures of various gases with impurity of solid and liquid particles. Between the components of such a mixture there can occur chemical reactions and mutual transformations.

When describing the behavior of combustion products it is considered that in the entire mixture each gas and the condensed particles keep their individuality. This assumption is spread to the behavior of ionized combustion products, which can be formed during application of advanced high-energy propellants or with the presence of substances with low thermal ionization potential in the composition of propellant.

In <u>homogeneous</u> gas mixture, not containing condensed particles, each component is assigned: individual partial pressure p_i, individual molecular weight μ_i or specific gas constant R_i, individual values of heat capacity C_{vi} and entropy S_i. However, temperature T and velocity of kinetic motion w in the studied molar volume of homogeneous gas mixture are considered identical for all the components.

Composition of such mechanical mixture of various gases is assigned in the following forms:

1) by concentration by weight

$$g_i = \frac{G_i}{\sum G_i};\tag{II.6}$$

2) by molar concentrations

$$c_i = \frac{N_i}{v};\tag{II.7}$$

3) by concentrations by volume r_i, representing the dimensionless ratio of number of moles of i component N_i to the number of moles of the entire mixture $N = \Sigma N_i$:

$$r_i = \frac{N_i}{N} = \frac{v_i}{v} = \frac{p_i}{p}.\tag{II.8}$$

To the entire homogeneous gas mixture there are assigned general parameters: pressure of mixture $p = \Sigma p_i$, volume of mixture $v = \Sigma v_i$, number of moles of all gases in the volume of the mixture $N = \Sigma N_i$, temperature T and velocity w.

Furthermore, the idea is introduced concerning some apparent molecular weight of the mixture, determined by formula

$$\mu = \frac{G}{N} = \sum \mu_i r_i = \frac{1}{p} \sum \mu_i p_i.\tag{II.9}$$

Universal gas constant R_μ = 1.985 cal/mole·deg is extended to all the homogeneous mixture, and specific gas constant of mixture R cal/kg·deg is calculated through apparent molecular weight of the mixture:

$$R = \frac{R_\mu}{\mu} = \frac{1,985p}{\sum \mu_i p_i}.\tag{II.10}$$

Entropy S, internal energy U and enthalpy I of all the homogeneous or heterogeneous mixture of combustion products are calculated on the basis of the property of energy additivity so:

For one mole   For one kilogram

$$S_\mu = \sum S_{\mu_i} r_i; \quad S = \sum S_i g_i = \frac{S_\mu}{\mu}; \qquad (II.11)$$

$$U_\mu = \sum U_{\mu_i} r_i; \quad U = \sum U_i g_i = \frac{U_\mu}{\mu}; \qquad (II.12)$$

$$I_\mu = \sum I_{\mu_i} r_i; \quad I = \sum I_i g_i = \frac{I_\mu}{\mu}. \qquad (II.13)$$

Heat capacity of reacting combustion products is determined in a somewhat more complicated manner, as is described in the following section.

In heterogeneous combustion products, containing solid and liquid particles, the condensed components differ from properties of gases. Therefore, parameters of the state of gaseous combustion products including solid and liquid phases, are calculated under the following additional assumptions.

1. Volumes occupied by solid or liquid phases are assumed equal to zero, since the content of these components in the overall volume of gaseous products is small, and their specific gravity is two-three orders greater as compared to gas. Such an assumption is identical to that, which disregards the volume of molecules themselves in ideal gases.

2. Partial pressures of solid and liquid particles in gasesous combustion products are also considered equal to zero.

3. Overall pressure in heterogeneous mixture is equal to the sum of partial pressures of gaseous components.

4. The gaseous part of heterogeneous mixture of combustion products satisfies equation of state for ideal gases.

5. Content of solid and liquid phases is estimated by their weight or molar concentration.

6. During calculations of equilibrium states it is assumed that solid particles are so small in dimensions that they succeed in acquiring the velocity and temperature of gas flow. It is considered that this assumption under liquid-propellant rocket engine conditions is justified with particle dimensions not exceeding $5 \cdot 10^{-3}$ mm.

With large dimensions of condensed particles there are performed comparative calculations in the assumption of limiting cases of nonequilibrium in heterogeneous mixture:

a) with thermal nonequilibrium between condensed particles and gas, when the temperature of solid and liquid particles does not follow changes of gas temperature and remains constant;

b) with dynamic nonequilibrium, when the velocity of condensed particles does not follow changes of gas velocity and remains constant.

The first of the assumptions that volume of condensed phase is equated to zero ($v_K = 0$), is sometimes not made. Then to equations of state there is introduced not the entire volume of mixture v, but the difference of volumes ($v - v_K$). With this there are obtained solutions admissible for use, although more complex.

The working medium as a thermodynamic system, separated from the environment by control surfaces, disposes various forms of internal motion of matter and, consequently, has determinate energy. It is accepted to call this energy internal.

It is rather difficult to find the absolute value of internal energy. However, for technical calculations it is important to know only the components of internal energy which participate during transformations of motions under liquid-propellant rocket engine conditions.

Such components in reacting combustion products are intenal thermal energy u and internal energy of physical or chemical transformations (change of state of matter, dissociation, ionization and so forth) of substances, which we will call chemical internal energy and designate by $U_{\text{хим}}$.

The measure of internal thermal energy u is temperature

$$du = c_v dT;$$

$$u = u_0 + \int_0^T c_v dT. \qquad (II.13')$$

where c_v – heat capacity of individual substance.

By internal chemical energy $U_{\text{хим}}$, of individual substance there is meant the heat of formation $Q_{\text{обр}}$ of given substance from certain parent substances, taken in conditional standard state. If heat is expended during formation of substance, then it is considered that internal energy of the forming substance is greater by the value of heat of formation.

Consequently, by total internal energy of individual substance, participating in transformation processes of motions under liquid-propellant rocket engine conditions, we will mean the sum of

$$U_i^{\text{полн}} = u_i + U_{\text{хим}\,i} = u_i + Q_{\text{обр}\,i}. \qquad (II.14)$$

Reference system of total internal energy for individual substances is constructed analogous to reference system of total enthalpies, examined in Chapter VI.

Total internal energy for one mole (one kilogram) of reacting combustion products can be calculated by equation (II.12).

On the other hand, analogous to (II.13') the change of total internal energy dU can be written through heat capacity of the entire mixture of reactants so

$$dU = c_v dT. \qquad (II.15)$$

Thus, change of total internal energy of the examined system with temperature is connected through heat capacity of the mixture of reactants c_v. This connection is simple only for equilibrium processes, when in accordance with temperature change the saturation of energy levels of atoms and molecules (energy equilibrium) is changed and reactions of dissociation occur until reaching chemical equilibrium between the composition of combustion products and temperature.

Value of heat capacity of reacting working medium, which connects the change of total internal energy with temperature change in equilibrium processes, is called equilibrium heat capacity.

In nonequilibrium processes the heat capacity can take different values depending on the degree of nonequilibrium.

During analyses of limiting cases of total chemical nonequilibrium, when the composition of gases does not follow the temperature change and remains constant, and into consideration of total energy nonequilibrium there is introduced the concept of so-called limiting nonequilibrium heat capacity, which is designated by c_v^* with indication of the form of nonequilibrium motion. Such heat capacity is sometimes called "frozen" heat capacity.

§ 2. Determination of Properties of Reacting Working Media

As was noted above, in final calculation formulas the properties of working media are described by values of gas constant R, values of heat capacities c_v and c_p, sound propagation velocity and index of adiabatic process, representing the ratio of heat capacities $k = c_p/c_v$.

Let us consider determination of these properties of reacting combustion products in reference to combustion chambers and nozzle boxes of liquid-propellant rocket engines.

Homogeneous Gas System

Heat capacity c_{v_i} for individual substances

$$c_{v_i} = \left(\frac{\partial U_i}{\partial T}\right)_{v=\mathrm{const}} \qquad \text{(II.16)}$$

is listed in tabular values of thermodynamic properties.

For a reacting gas mixture the value of equilibrium heat capacity c_v can be determined by proceeding from the idea of total internal energy:

$$c_v = \left(\frac{\partial U}{\partial T}\right)_{v=\mathrm{const}}. \qquad \text{(II.17)}$$

On the basis of (II.12) for one mole (N = 1) it is possible to write

$$c_v = \sum\left[\frac{\partial (U_i r_i)}{\partial T}\right] = \sum\left[\left(\frac{\partial U_i}{\partial T}\right)_v r_i + U_i\left(\frac{\partial r_i}{\partial T}\right)_v\right]. \qquad \text{(II.18)}$$

Whence we obtain the final formula for determining equilibrium heat capacity of one mole of reacting combustion products

$$c_v = \sum c_{v_i} N_i + \sum U_i\left(\frac{\partial N_i}{\partial T}\right)_v. \qquad \text{(II.19)}$$

In this formula c_{v_i} and U_i are tabular values of heat capacity and internal energy of individual substances.

In the entire reacting mixture there occurs change of the number of moles of components N_i due to chemical reactions or other transformations. Therefore, in equation (II.19) values of N_i enter under the sign of derivative

$$\left(\frac{\partial N_i}{\partial T}\right)_{v=\mathrm{const}}.$$

Thus, for determination of equilibrium value of heat capacity of the reacting thermodynamic system c_v, besides tabular values of c_v and U, for individual components it is preliminary required to find the mixture ratio, assigned by N_i, and values of partial derivatives $\left(\frac{\partial N_i}{\partial T}\right)_v$ for each component.

Methods of finding the composition of reacting working medium and values of partial derivatives of type $\left(\frac{\partial N_i}{\partial T}\right)_v$ are discussed in Chapter VI during calculations of combustion in the chamber and outflow of combustion products from the nozzle box.

It is simple to note that with constant composition of working medium μ = const and $\frac{\partial N_i}{\partial T} = 0$ the second term in equation (II.19) vanishes.

Consequently, when in the method of calculations it is assumed to estimate the limiting case of complete chemical nonequilibrium or we are concerned with ideal nonreacting gases, then for this case the heat capacity of the mixture will be determined so:

$$c_v^0 = \sum c_{v_i} N_i^0. \qquad \text{(II.20)}$$

Here in the sense of N_i^* the constants and such heat capacity of the mixture can be called heat capacity of the chemically frozen process.

In calculation practice for determining the equilibrium heat capacity of reacting combustion products we most frequently use approximate formula

$$\overline{c_v} = \sum c_{v_i} N_i. \qquad \text{(II.21)}$$

which differs from exact equation (II.19) by the fact that for simplification of calculations there is dropped the term containing partial derivative of form $\left(\frac{\partial N_i}{\partial T}\right)_v$, however the composition of gas, determined by values of N_i = var, is taken variable, changing stably.

This gets rid of the necessity of finding partial derivatives, which gets rid of half the labor input for calculating the composition of combustion products.

Tabular values of heat capacity c_{v_i} and internal energy U_i for individual components of the mixture correspond to energy equilibrium conditions over all the energy levels of molecules and atoms of this substance. Moreover, in thermal processes there appears total heat capacity of the given individual substance c_{v_i}, which is composed of heat expenditures for different types of intramolecular and intratomic motions in atoms and molecules of this substance:

$$c_{v_i} = c_{i\,\text{поступ}} + c_{i_\text{вращ}} + c_{i_\text{колеб}} + c_{i_\text{эл}} + \cdots \qquad \text{(II.22)}$$

Limiting energy nonequilibrium is the name for the process of intramolecular motion when, besides forward motion and rotation of molecules $c_{i_\text{пост}}$ and $c_{i_\text{вращ}}$, all other energy levels (oscillations of atoms $c_{i_\text{колеб}}$, electronic levels $c_{i_\text{эл}}$ and so forth) are not excited and turn out to be as if "frozen," i.e., are not participating in the process.

Then heat capacity of the individual substance, manifested in the limiting energy nonequilibrium process, will comprise only the sum of two components

$$c^{*}_{v_i} = c_{i_\text{пост}} + c_{i_\text{вращ}}. \qquad \text{(II.23)}$$

With sufficient accuracy $c^{*}_{v_i}$ can be estimated by the molecular-kinetic theory of heat capacity:

$$c^{*}_{v_i} = \frac{R_{\mu}}{2}\left(i_\text{пост} + i_\text{вращ}\right) = \frac{1.985}{2}\left(i_\text{пост} + i_\text{вращ}\right), \qquad \text{(II.24)}$$

where $i_\text{пост}$ — number of steps of forward motions ($i_\text{пост} = 3$); $i_\text{вращ}$ — number of steps of rotations, which depends on atomicity and the structure of molecules.

Consequently, when in the method of appraisal calculations it is proposed to examine the limiting case of total chemical nonequilibrium and simultaneously total energy nonequilibrium of intramolecular motions, then for this case it is necessary to take the heat capacity of the double form of nonequilibrium for gas mixture

$$c_v^{\bullet\bullet} = \sum c_{v_i}^{\bullet} N_i^{\bullet}. \tag{II.25}$$

Value of heat capacity at constant pressure c_p for reacting gases can be determined analogously, as for heat capacity at constant volume, with the difference that instead of total internal energy U is considered total enthalpy of working medium I:

$$c_p = \left(\frac{\partial I}{\partial T}\right)_{p=\text{const}}. \tag{II.26}$$

Corresponding calculation formulas will take the following expressions:

$$c_p = \sum c_{p_i} N_i + \sum I \left(\frac{\partial N_i}{\partial T}\right)_{p=\text{const}}; \tag{II.27}$$

$$\bar{c}_p = \sum c_{p_i} N_i; \tag{II.28}$$

$$c_p^{\bullet} = \sum c_{p_i} N_i^{\bullet}; \tag{II.29}$$

$$c_p^{\bullet\bullet} = \sum c_{p_i}^{\bullet} N_i^{\bullet}. \tag{II.30}$$

The Meyer formula is known in thermodynamics; it connects the difference of heat capacities c_p and c_v with the value of gas constant R_μ. It should be borne in mind that this formula is accurate only for ideal nonreacting gases or in the case of limiting chemical nonequilibrium, therefore it can be written:

$$c_p^{\bullet} - c_v^{\bullet} = R_\mu = 1{,}985\ \frac{\text{kcal}}{\text{mole}\cdot\text{deg}} \tag{II.31}$$

For equilibrium heat capacities in reacting gas the exact expression of this formula for one mole of mixture will be

$$c_p - c_v = R_\mu = (\bar{c}_p - \bar{c}_v) + \left[\sum I_i \left(\frac{\partial N_i}{\partial T}\right)_p - \sum U_i \left(\frac{\partial N_i}{\partial T}\right)_v\right]. \qquad \text{(II.32)}$$

If we use approximate formulas (II.21) and (II.28) for calculation of equilibrium heat capacities in reacting gas, then it is possible to write that with the same approximation

$$\bar{c}_p - \bar{c}_v = R_\mu = 1{,}985. \qquad \text{(II.33)}$$

Ratio of heat capacities k = $\frac{c_p}{c_v}$, important for the use of thermodynamic formulas, will differ, depending on calculation conditions, just as equilibrium and "frozen" heat capacities differ.

Exact expression of this index for equilibrium processes in reacting gases will be

$$k = \frac{c_p}{c_v} = \frac{\bar{c}_p + \sum I_i \left(\frac{\partial N_i}{\partial T}\right)_p}{\bar{c}_v + \sum U_i \left(\frac{\partial N_i}{\partial T}\right)_v} \text{ for one mole.} \qquad \text{(II.34)}$$

If we use approximate formulas for equilibrium heat capacities (II.21) and (II.28), then the approximate value of $\bar{k}$ in this case will be

$$\bar{k} = \frac{\bar{c}_p}{\bar{c}_v} = \frac{\sum c_{p_i} N_i}{\sum c_{v_i} N_i} = 1 + \frac{1{,}985}{\bar{c}_v}. \qquad \text{(II.35)}$$

For limiting nonequilibrium processes

$$k^* = \frac{\dot{c}_p}{\dot{c}_v} = 1 + \frac{1.985}{\dot{c}_v}; \quad k^{**} = \frac{\ddot{c}_p}{\ddot{c}_v} = 1 + \frac{1.985}{\ddot{c}_v}. \qquad \text{(II.36)}$$

<u>Velocity</u> of sound a is determined by relationship

$$a^2 = \left(\frac{\partial p}{\partial \rho}\right)_s, \qquad \text{(II.37)}$$

where index s indicates the constancy of entropy.

Exact expression for velocity of sound in equilibrium reacting combustion products will be

$$a^2 = \bar{k} g R T \frac{1+\mu T\left(\frac{\partial N}{\partial T}\right)_s}{1+\mu T\left(\frac{\partial N}{\partial T}\right)_p}. \tag{II.38}$$

where $R = \frac{848}{\mu}$ – specific gas constant of mixture in kg·m/kg·deg.

By disregarding the terms with partial derivatives, we will obtain the approximate value of magnitude $\bar{a}$:

$$\bar{a}^2 = \bar{k} g R T. \tag{II.39}$$

Accordingly for limiting nonequilibrium processes

$$(a^*)^2 = k^* g R^* T; \quad (a^{**})^2 = k^{**} g R^* T, \tag{II.40}$$

where $R^* = \frac{848}{\mu^*}$ – specific gas constant, calculated by molecular weight of the mixture of "frozen" chemical composition.

Figure II.2 shows change of equilibrium heat capacity of hydrogen depending on the temperature at various pressures, in accordance with exact formula (II.27) – solid curves. As can be seen on the graph, equilibrium heat capacity of reacting gas c_p sharply increases in the region of intense dissociation and reaches maximum value where there occurs the most intense change of number of moles when $\left(\frac{\partial N}{\partial T}\right) = \max$. The dashed line on this figure shows change of heat capacity $\bar{c}_p$ according to approximate formula II.28.

In figure II.3 as an example there is shown change of other physical properties during dissociation and ionization of hydrogen for pressures 10 [atm(abs.)]. In regions of intense dissociation and intense ionization for hydrogen index k turns out to be less than $\bar{k}$ by 20-25%, and velocity of sound a is less than $\bar{a}$ by 10-15%.

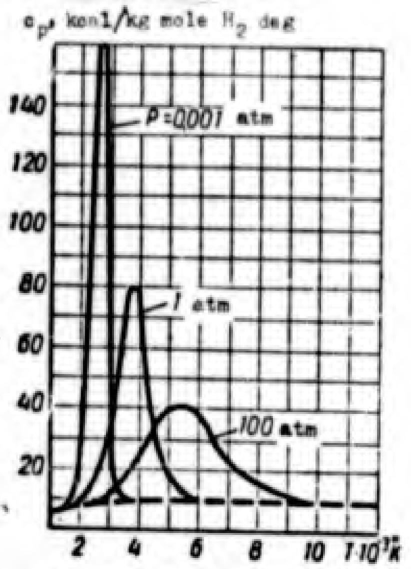

Fig. II.2. Change of heat capacity of dissociating hydrogen, taken in a quantity of 1 mole of initial molecular hydrogen.

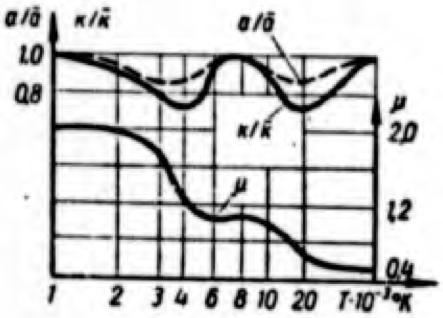

Fig. II.3. Comparison of equilibrium values of thermodynamic properties of dissociating or ionizing hydrogen at various temperatures, determined by exact formula (a and κ) and by approximate formula ($\bar{a}$ and $\bar{\kappa}$).

During calculations of gas exit velocity from the nozzle w and specific engine thrust with the use of exact value of k or approximate value of $\bar{k}$ the difference in calculations can be 0.5-1.0%.

Absolute values of heat capacity c_p according to exact formula and $\bar{c}_p$ according to approximate formula, as can be seen on Fig. II.2, can differ by several times. However, absolute values of heat capacities do not directly enter calculation formulas for specific thrust. The large difference of c_p and $\bar{c}_p$ can essentially affect calculations on heat exchange in reacting gases, where this circumstance should be emphasized.

Properties of Heterogeneous Combustion Products

During assumptions with respect to the behavior of heterogeneous mixtures, specified in § 1, heat capacities of the entire mixture of reacting combustion products, containing solid and liquid particles, can be calculated by the same formulas as for homogeneous mixtures, which are examined above. In reference to heterogeneous working media the overall heat capacity of the entire mixture c_s is split into two parts: heat capacity of all condensed particles c_k. If we designate the content of all condensed particles by concentration by weight g_k, then for specific gravity heat c_s of heterogeneous mixture

$$c_{v_s} = (1 - g_k)c_v + g_k c_k; \qquad \text{(II.41)}$$

$$c_{p_s} = (1 - g_k)c_p + g_k c_k. \qquad \text{(II.42)}$$

If in the rapidly occuring processes of change of the parameters of gas state the solid particles do not entirely change their temperature, then this suggests limiting thermal nonequilibrium of motion of condensed phase. In this case the heat capacity of solid phase drops from equations (II.41) and (II.42), and they acquire the following appearance:

$$\left(c_{v_s}\right)' = (1 - g_k)c_v;$$

$$\left(c_{p_s}\right)' = (1 - g_k)c_p. \qquad \text{(II.43)}$$

Gas constant in the presence of condensed phase

$$R_s = c_{p_s} - c_{v_s} = (1 - g_k)R. \qquad \text{(II.44)}$$

At thermal nonequilibrium of condensed phase the gas constant

$$(R_s)' = \left(c_{p_s}\right)' - \left(c_{v_s}\right)' = (1 - g_k)R.$$

In the case of propagation of action of usual gas-dynamic equations to flow of heterogeneous mixtures let us write expression for adiabatic index k_s in such a mixture. From formulas (II.41), (II.42), and (II.44) we obtain

$$k_s = \frac{c_{p_s}}{c_{v_s}} = 1 + \frac{1 - g_k}{1 - g_k\left(1 - \frac{c_k}{c_v}\right)} \cdot \frac{R}{c_v}. \qquad \text{(II.45)}$$

With limiting thermal nonequilibrium of motion of condensed phase

$$k_s^* = \frac{c_p^*}{c_v} = \frac{c_p}{c_v} = k. \qquad \text{(II.46)}$$

Real flows of heterogeneous combustion products are characterized by the average value of the relationship of k_{cp} between k_s and k. Velocity of sound in such mixtures is determined by the gas phase.

§ 3. Equations of State of Working Media

In spite of the presence of chemical reactions, it is assumed that gaseous working media satisfy equation of state of ideal gas in the form

$$pV = NR_\mu T, \qquad \text{(II.47)}$$

where R_μ – universal gas constant, equal to 1.985 kcal/mole·deg. This equation is extended to the entire homogeneous gas mixture.

In such a mixture for each individual gas in conditions of equilibrium it is possible to write the particular equation of state so:

$$p_i V = N_i R_\mu T, \qquad \text{(II.48)}$$

where N_i – number of moles of i component.

In these equations for reacting gases the number of moles N is variable, and in differential form the equation of state will look so:

$$\frac{dp}{p} + \frac{dV}{V} - \frac{dN}{N} - \frac{dT}{T} = 0. \qquad \text{(II.49)}$$

In particular cases of ideal nonreacting gas or with extreme chemical nonequilibrium in reacting gas dN = 0, and then

$$\frac{dp}{p} + \frac{dV}{V} = \frac{dT}{T}. \qquad \text{(II.50)}$$

Frequently in calculations it is convenient to operate by <u>specific</u> parameters of state, pertaining to one kilogram of working medium

$$v = \frac{V}{N\mu}; \quad \gamma = \frac{1}{v}; \quad R = \frac{R_\mu}{\mu}.$$

Through specific parameters the equation of state is written so:

$$pv = \frac{R_\mu}{\mu} T \quad \text{or} \quad pv = RT, \qquad \text{(II.51)}$$

and in differential form

$$\frac{dp}{p} + \frac{dv}{v} + \frac{d\mu}{\mu} = \frac{dT}{T}. \qquad \text{(II.52)}$$

For generality of solutions the behavior of gaseous combustion products, containing solid and liquid particles (heterogeneous media), describe the same mathematical form of equation of state as for ideal gases. This becomes possible during assumptions in connection with properties of heterogeneous systems, stipulated above in § 1 of this chapter, and also taking into account equation (II.44).

In this case for heterogeneous mixtures

$$pv = R_s T = (1 - g_K) RT. \qquad \text{(II.53)}$$

where R_s – specific gas constant for heterogeneous combustion products according to equation (II.44).

With the shown assumptions it is considered that volume of condensed phase $v_K = 0$.

To a certain degree the influence of concentration of condensed phase g_K can be taken into consideration if the assumption is taken that $v_K = 0$. Then it will be necessary to write the volume of gaseous phase in equation (II.53) in the form of the difference of $(v - v_к)$, and the entire equation will be copied in the form

$$p\left(1 - g_к \frac{\gamma_s}{\gamma_к}\right) = \gamma_s R_s T. \qquad (II.54)$$

where γ_s – specific gravity of the entire heterogeneous mixture; $\gamma_к$ – specific gravity of substance of condensed phase.

In some cases, for example during calculations of throttling devices on gas lines, for exposure of Jule-Thomson effect, and also during calculations of vapor flow under conditions close to the saturation line, it is necessary to resort to more accurate equations of the state of real gases and vapors such as van der Waals equations.

Besides the value of gas constant R, in van der Waals equation of property of gases there are even considered coefficients a and b:

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT. \qquad (II.55)$$

Coefficients a and b are constants, depending on the nature of working medium, but not on parameters of state.

Usually these coefficients are determined for each gas through its critical parameters $p_{крит}$ and $T_{крит}$ taking into account gas constant R in the following way:

$$a = \frac{27}{64} R^2 \left(\frac{T}{p}\right)_{крит} \text{ and } b = \frac{1}{8} R \left(\frac{T}{p}\right)_{крит}. \qquad (II.56)$$

Values of critical parameters are listed in tabular data.

§ 4. Phenomena of Motion Transfer in Liquid-Propellant Rocket Engine Conditions

Along the ducts of liquid-propellant rocket engine propulsion systems there occur transformations of various types of motion of matter. For quantitative appraisal of each type of motion there is the same measure – energy. Thus, energy is a single property of matter and all forms of motion. During mutual transformations of various forms of motion the energy remains constant.

However, inasmuch as to energy, measuring the concrete forms of motion, there are assigned corresponding names (kinetic energy, mechanical work, thermal energy or simply heat, chemical energy and so forth), then instead of transformation of forms of motion we more frequently indicate conversion of one form of energy into another. Such terminology will be used further.

Conversions of energy in various propulsion systems are examined on the basis of two thermodynamic methods: method of <u>cycles</u> (in reference to periodically operating machines) and method of <u>flows</u> (in reference to continuous conversion processes).

The second method of flows is more inherently connected with conditions in ZhRD propulsion systems. Therefore, the following discussion of fundamentals of thermodynamic calculations is based on the study of method of flows and transfer of motion forms.

<u>Phenomenon of transfer of substance or propagation of corresponding type of motion into the space or volume of the considered medium is called flow</u>.

As basic flow in liquid-propellant rocket engine conditions we consider motion of the mass of working medium along propulsion system ducts and in combustion chamber. Working medium is a carrier of several noticeable forms of motion of matter at once. Therefore, simultaneously with mass transfer of substance there is carried out transfer of types of motion peculiar to this mass, i.e., forms of energy.

Thus, conversion of forms of energy into each other occurs in flows, connected with transfer of mass of working medium along ducts and different forms of energy. Furthermore, through walls of channels or with the aid of units inserted in the basic flow there can be carried out interaction of working medium with environment. These interactions are considered as transfer of corresponding forms of motion from the working medium to the environment, or conversely.

Inside the studied volume of working medium flows can be considered as transfer phenomenon (interchange of various forms of motion by energy) between separate phases or particles, making up this medium.

§ 5. Energy Dissipation During Transfer Phenomena

For any motion the presence of conjugate physical quantites is obligatory: propulsion force (potential) P_1 and parameters of state (coordinates) X_1. Spontaneous transfer of mass or some form of motion of matter always occurs in the direction of decrease of corresponding propulsion force (potential) P_1.

A condition of any spontaneous transfer in the direction ℓ is the presence of propulsion force gradient

$$\frac{dP_i}{dl} + 0. \qquad (II.57)$$

Thus, for example, flow of gas or liquid in the pipeline occurs in the direction of decrease of propulsion force – pressure p, i.e., with the presence of pressure gradient along the length of the pipeline $\frac{dp}{dl}$. Heat transfer in a solid body by thermal conductivity occurs in the direction of temperature decrease with the presence of gradient $\frac{dT}{dl}$.

Any transfer and transformation of energy are connected with *dissipation* phenomenon, which consists of the fact that all forms of energy during transfers and mutual transformations of forms of motion partially or completely change into thermal form of motion. This phenomenon is called *internal* friction, inherent to each form of motion.

A single measure of dissipation for any motion is so called generalized work of dissipative forces

$$dL_{\text{диссип}} = P_i dX_i . \qquad \text{(II.58)}$$

This work $dL_{\text{диссип}}$ is always negative; it changes into heat $Q_{\text{диссип}}$, called dissipation heat:

$$dQ_{\text{диссип}} = -dL_{\text{диссип}} . \qquad \text{(II.59)}$$

In an overwhelming majority of cases dissipation heat $Q_{\text{диссип}}$ goes into increase of internal thermal energy of the working medium. Only in certain cases can dissipation heat be discharged into the environment.

Dissipation heat provides part of the useful forms of energy, changing them back into heat. The same role is played by friction on the walls of channels: the work of friction forces on the walls of channels $dL_{\text{тр}}$ changes into heat $Q_{\text{тр}}$.

Both these phenomena lead to increase of entropy along the gas flow path, which can be estimated so:

$$dS_{\text{диссип}} = \frac{dQ_{\text{диссип}} + dQ_{\text{тр}}}{T} . \qquad \text{(II.60)}$$

Thus, in real cases flows always occur with increase of entropy, even if friction of working medium against channel walls is disregarded.

§ 6. General Form of Equation of Conservation of Energy

In the theory of motion of working media along the ducts of liquid-propellant rocket engine propulsion systems there is considered stabilized one-dimensional flow.

For the study of overall interconnections during transformations of energy in flow let us use a fixed system of coordinates, connected with the channel walls, about which the working medium as a continuous medium has velocity w.

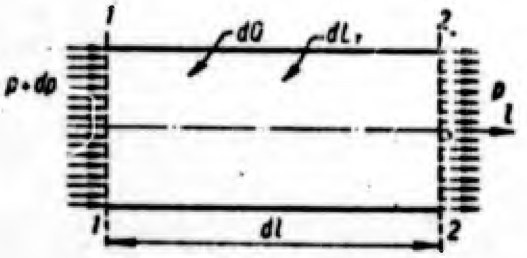

Fig. II.4. Diagram of motion of working medium in channel.

For description of the flow of working medium in channel we will select the thermodynamic system, limited on Fig. II.4 by solid walls of channel and control sections 1-1 and 2-2.

While formulating the equation of conservation of energy we will consider the following types of generalized operations in various forms of motion:

1. Mechanical extrusion of mass of working medium along the channel was without taking into account compressibility, carried out due to the difference of ambient pressures dp at channel entrance and exit. Work of extrusion dG (kg) of working medium will be

$$dL'_{\text{тр}} = Pdx = Fdpdx = dVdp.$$

For one kilogram

$$dL_{\text{тр}} = \frac{dL'_{\text{тр}}}{dG} = vdp.$$

2. Work of deformation (compression or expansion)

$$dL'_{\text{деф}} = pdV, \text{ and for 1 kg } dL_{\text{деф}} = pdv.$$

3. Generalized work of chemical transformations of components, making up the working medium:

for 1 mole of individual substance

$$dL'_{\text{хим}} = \chi_i dN_i;$$

for 1 mole of mixture of substances

$$dL'_{\text{хим}} = \sum \chi_i dN_i;$$

for 1 kg of working medium

$$dL_{\text{хим}} = \frac{1}{\mu} \sum \chi_i dN_i.$$

4. External thermal influence through channel walls

$$dL_Q = dQ = Tds,$$

where s — specific value of entropy for 1 kilogram.

5. External mechanical influence in the form of technical work, carried out by special devices (compressor or turbine) on path dl: for 1 kg of working medium $dL_{\text{т}}$.

6. Generalized work of kinetic motion (kinetic energy) of mass m

$$dL'_{\text{кин}} = wdk = wd(mw) = d\left(\frac{mw^2}{2}\right);$$

for 1 kg of working medium

$$dL_{\text{кин}} = d\left(\frac{w^2}{2g}\right).$$

7. Work of dissipation $\Sigma dL_{\text{диссип}}$ and work of friction against wall $\Sigma dL_{\text{тр}}$ on section dl for 1 kg of working medium.

8. Corresponding heats of dissipation $\Sigma dQ_{\text{диссип}}$ and friction against walls $\Sigma dQ_{\text{тр}}$.

9. Change of internal energy of thermal motion du. General law of conservation of energy according to equation (II.5)

$$dU = \sum dL_i$$

in the examined case taking into account terminology of signs of work and heat[1] will be written in the following way:

$$du + dL_{\text{хим}} = -dL_{\text{пр}} - dL_{\text{деф}} + dQ - dL_{\text{т}} - dL_{\text{кин}} - \\ -\sum dL_{\text{диссип}} + \sum dQ_{\text{диссип}} - \sum dL_{\text{тр}} + \sum dQ_{\text{тр}} \qquad \text{(II.61)}$$

or

$$du + \frac{1}{\mu} \sum \chi_i dN_i = -vdp - pdv + Tds - dL_{\text{т}} - d\left(\frac{w^2}{2g}\right)^2. \qquad \text{(II.62)}$$

In these equations the works and heats of dissipation and friction can be omitted on the basis of (II.59).

While applying the concept of total internal energy according to equation (II.14) for reacting working media, let us rewrite formula (II.62):

$$dU = -vdp - pdv + Tds - dL_{\text{тр}} - d\left(\frac{w^2}{2g}\right). \qquad \text{(11.63)}$$

---

[1] Heat imparted to working medium is considered positive, and work negative.

This equation of conservation of energy in flows is even more simplified if we consider that

$$vdp + pdv = d(pv),$$

and the sum of

$$dI = dU + d(pv) = d(U + pv)$$

represents change of <u>total</u> enthalpy.

With introduction of function of total enthalpy we will obtain

$$dI = Tds - dL_{\text{т}} - d\left(\frac{w^2}{2g}\right). \qquad \text{(II.64)}$$

Limiting simplification of writing the equation of energy for flows is attained with the use of function I_0, called <u>total enthalpy of stagnation</u>:

$$I_0 = U + pv + \frac{w^2}{2g}. \qquad \text{(II.65)}$$

Then instead of (II.64) it is possible to write

$$dI_0 = Tds - dL_{\text{т}}, \qquad \text{(II.66)}$$

and in the absence of technical work and heat exchange through walls ($dQ = 0$ and $dL_{\text{т}} = 0$) there will be satisfied condition

$$dI_0 = 0, \quad \text{or} \quad I_0 = \text{const}. \qquad \text{(II.67)}$$

Sometimes for the description of processes in flows of working media we use a <u>transient coordinate system</u>, connected with the center of mass of the moving volume and travelling along the flow with the center of mass.

In such a coordinate system the equation of energy for moving working medium (II.63) will be

$$dU = -pdv + Tds + dQ_{диссип} \qquad (II.68)$$

or

$$dI = +vdp + Tds + dQ_{диссип}. \qquad (II.69)$$

Here in the right part of the equation for moving gas there is considered heat $dQ_{диссип}$ from dissipation of kinetic energy and displacement work, since these works themselves do not take part in the fixed system of coordinates.

For quiescent ($W = 0$), but for reacting the equation of conservation of energy will be

$$dU = -pdv + Tds \qquad (II.70)$$

or

$$dI = vdp + Tds. \qquad (II.71)$$

As compared to equation (II.70) the presence of dissipation heat in the right side of equation (II.68) distinguishes the flow of working medium from processes in the closed fixed volume of the same medium.

The application of equations (II.68) and (II.69), written in fixed system of coordinates, for the study of flows permits describing processes of internal transformations, while not going into details about mechanical and kinematic phenomena of displacement.

§ 7. Mechanical Form of Equation of Conservation of Energy

By subtracting equation (II.64) from equation (II.69), there can be obtained the formula of law of conservation of energy, which will contain only generalized works of some mechanical influences:

$$vdp + dL_т + d\left(\frac{w^2}{2g}\right) + dQ_{диссип} = 0. \qquad (II.72)$$

Such a formula is called Bernoulli equation or equation of "kinetic energy". The application of mechanical form of law of conservation of energy permits describing the mechanical motion, while not touching the details of internal transformations of working medium.

Integral form of Bernoulli equation

$$\int_1^2 vdp + L_{т}^{1-2} + \frac{w_2^2 - w_1^2}{2g} + Q_{\text{сопрот}}^{1-2} = 0. \qquad \text{(II.73)}$$

Difficulties in the application of Bernoulli equation consist of the fact that for determination of integral $\int_1^2 vdp = -\int_2^1 vdp$ by process 1-2 (see Fig. II.4) it is necessary to have a mathematical description of the process (equation of polytropic type process, where index n is frequently unknown). At the same time, with integration of total equation of conservation of energy (II.64) the necessity of determining index of process n drops.

In a particular case for incompressible liquid ($dv = 0$) the Bernoulli equation is easily integrated

$$p_1v_1 + \frac{w_1^2}{2g} - L_{т}^{1-2} = p_2v_2 + \frac{w_2^2}{2g} + Q_{\text{сопрот}}^{1-2}. \qquad \text{(II.73')}$$

Formula (II.73') can be used with satisfactory approximation during calculation of gas flow, if the flow velocity does not exceed 0.3 of the velocity of sound, i.e., when it is possible to disregard gas compressibility.

§ 8. Equations of Thermodynamic Process

In any applicable system of coordinates from generalized physical parameters $P_i - X_i$ the thermodynamic process can be illustrated by a certain curve $P_i = f(X_i)$. This curve will represent a continuous totality of states, through which the working medium passes in the described process (see Fig. II.1).

For two ideal processes, such as isothermal ($dT = 0$) and isentropic ($dS = 0$), if we disregard energy dissipation the mathematical form of equation of curve $p = f(v)$ can be obtained in the following form:

$$pv^n = \text{const}, \qquad (II.74)$$

where n – index of the process, equal to one (when $dT = 0$) and ratio $k = c_p/c_v$ during isentropic change of parameters of states ($ds = 0$).

Such mathematical form of equation is extended to the description of real processes, for this we operate by certain mean values of indices n_{cp}.

Averaging of the value of index n between two states 1-2 is usually performed by formula

$$n_{cp} = \frac{\lg p_2/p_1}{\lg v_1/v_2} = \frac{\lg p_2/p_1}{\lg\left(\frac{p_2}{p_1}\cdot\frac{T_1}{T_2}\cdot\frac{R_1}{R_2}\right)}. \qquad (II.75)$$

For reacting combustion products the specific gas constants R_1 and R_2 in equation (II.75) should not be reduced, since this will be accompanied by additional errors in view of inequality $R_1 \neq R_2$.

As is shown visually on Fig. II.5, the use of curve a, drawn on the basis of equation (II.74) with mean value of index n_{cp} as compared to the real course of the process on curve b, introduces errors in determining the intermediate parameters of state and the value of work L.

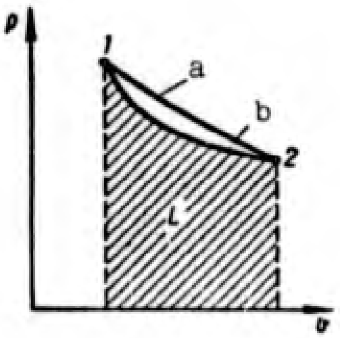

Fig. II.5. Image of the process in coordinates p-v and T-s: (a) according to equation (II.74) for polytrope with average index and (b) the real process.

Sometimes for detailed analysis, for example when determining the exact location of transition of subsonic flow into supersonic, the curve of the real process in coordinates p-v, as is shown on Fig. II.6, is represented in the form of successive totality of elementary polytropes with various indices n.

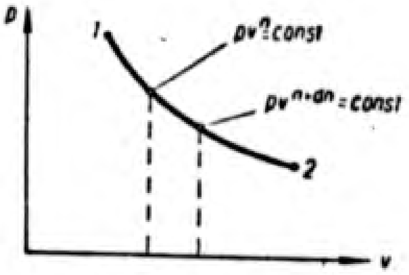

Fig. II.6. Image of real process in the form of totality of polytropes with variable index.

With such an approach to description of the real process the working medium in each state should satisfy both equation of state $pv = RT$, and simultaneously equation (II.74) with local value of index n. Along with this, index n along the path of the process is assumed variable.

§ 9. Equation of Continuity of Flow of Working Medium

This equation is an expression of the law of continuity and conservation of matter.

Velocities of displacements of working medium in liquid-propellant rocket engines in relation to propagation velocity of light are very small, therefore relativistic change of mass in gas flows will be completely disregarded. Then for any section it is possible to write that the arrival of mass per second is equal to its discharge

$$dm = d(w\rho F) \tag{II.76}$$

or in expanded form

$$\frac{dw}{w} + \frac{dF}{F} + \frac{d\rho}{\rho} = \frac{dm}{m}. \tag{II.77}$$

In steady state of flow at constant flow rate of working medium per second dm = 0. Then the equation of continuity will be written:

$$\frac{dw}{w}+\frac{dF}{F}+\frac{d\rho}{\rho}=0, \qquad \text{(II.78)}$$

or

$$\frac{dw}{w}+\frac{dF}{F}-\frac{dv}{v}=0. \qquad \text{(II.79)}$$

This equation permits connecting geometric dimensions of the channel with flow parameters of the working medium.

§ 10. Equation of Momentum

Equation of change of momentum

$$Pd\tau=d(mw), \qquad \text{(II.80)}$$

where P – sum of projections of all forces applied to the moving body to the direction of channel axis.

In reference to flows of liquids and gases another (hydrodynamic) form of such equation is more convenient which can be obtained the simplest of all from expression of law of conservation of energy. For this purpose we will apply Bernoulli equation (II.72) to flow, in which through cross-section area F in 1 s there flows 1 kg of working medium:

$$vdp+dL_{\tau}+d\left(\frac{w^2}{2g}\right)+dQ_{\text{диссип}}=0.$$

This will be the expanded form of equation of change of momentum. Considering that $v=\frac{1}{\gamma}$, and $\rho=\frac{\gamma}{g}$, let us rewrite this formula so:

$$dp+\gamma dL_{\tau}+\gamma dQ_{\text{тр}}+\rho w dw=0, \qquad \text{(II.81)}$$

where $dL_{\text{т}}$ and $dQ_{\text{тр}}$ – mechanical (external work) and friction heat, referred to 1 kg of working medium:

$$dp + \rho dL_{\text{т}} + \rho dQ_{\text{тр}} + \rho w dw = 0, \qquad \text{(II.82)}$$

where $dL_{\text{т}}$ and $dQ_{\text{тр}}$ are referred to a unit of mass of working medium.

External work $dL_{\text{т}}$ and friction work $dQ_{\text{тр}} = -dL_{\text{тр}}$ per second on length of channel dl can be expressed through corresponding forces and displacement per second (velocity):

$$dL_{\text{т}} = dPw;$$
$$dQ_{\text{тр}} = dP_{\text{тр}}w,$$

where P – projection of forces from the shifting solid walls of the machine, imparting external work to the flow. In accordance with the accepted terminology on sign of work, forces applied to flow of working medium by machine walls are considered negative; $P_{\text{тр}}$ – projection of friction forces to section dl.

After these conversions the equation of change of momentum will take the form

$$dp + \rho w dP + \rho w dP_{\text{тр}} + \rho w dw = 0. \qquad \text{(II.83)}$$

In the absence of external work and by allowing the absence of friction, it is possible to write:

$$dp + \rho w dw = 0. \qquad \text{(II.84)}$$

An important feature of the equation of momentum consists of the fact that with its help the effective forces are calculated with the use of only states of flow on the control surface without penetrating the essence of the processes occurring inside the volume of working medium, limited by these surfaces.

§ 11. Equations of Stagnation Parameters

With stagnation of flow of working medium the kinetic energy can change into potential energy of the working medium, into mechanical work and heat discharged outside. The case when flow is completely stopped ($w = 0$) and all the kinetic energy is transformed into potential energy of the working medium without losses into the environment, i.e., when external work is not accomplished and there is no heat exchange through channel walls, is called ideal stagnation.

For appraisal of potential energy reserves in flows it is convenient to take parameters of working medium during ideal stagnation as parameters of state. These stagnation parameters will be designated by the subscript zero, for example: I_0, T_0, p_0, ρ_0, etc.

It is simple to determine ideal temperature stagnation by total stagnation enthalpy I_0 on the basis of (II.26)

$$T_0 = \frac{I_0}{c_p} = \frac{c_pT + \frac{w^2}{2g}}{c_p} = T + \frac{w^2}{2gc_p}. \qquad \text{(II.85)}$$

If for calculation of equilibrium heat capacities c_p and c_v of reacting combustion products we use approximate formulas (II.21) and (II.29), then on the basis of (II.33) and (II.35) it is possible to write

$$\bar{c}_p = \frac{\bar{k}}{\bar{k}-1} R. \qquad \text{(II.86)}$$

Then by introducing thermodynamic temperature T in parentheses in equation (II.85) and using (II.86), we obtain

$$T_0 = T\left(1 + \frac{\bar{k}-1}{2} \frac{w^2}{\bar{k}gRT}\right).$$

By replacing velocity of sound $a^2 = \bar{k}gRT$, in it according to equation (II.39), and also introducing number $M = \frac{w}{a}$, we obtain

$$T_0 = T\left(1 + \frac{\bar{k}-1}{2} M^2\right). \qquad \text{(II.87)}$$

It is possible to trace the change of stagnation temperature along flow on the basis of equation of conservation of energy in the form (II.66)

$$dI_0 = Tds - dL_T.$$

Whence it follows that with the absence of external mechanical work ($dL_T = 0$) and heat exchange through walls ($Tds = dQ = 0$) there will be satisfied condition of constancy of stagnation temperature along the flow path:[1]

$$T_0 = T\left(1 + \frac{\bar{k}-1}{2} M^2\right) = \text{const}. \qquad \text{(II.88)}$$

Here it is appropriate to note that with isolation of working medium from interactions with the environment through channel walls friction does not affect stagnation temperature T_0. It will affect only thermodynamic temperature T, increasing it due to decrease of kinetic energy. This is found in accordance with law of conservation of energy.

Ideal stagnation pressure can be determined by Bernoulli equation (II.73)

$$\int_1^2 vdp + \frac{w_2^2 - w_1^2}{2g} + Q^{1-2}_{\text{внешн}} = 0.$$

In the absence of heat exchange with the environment, according to adiabatic equation

$$\int_p^{p_0} vdp = \frac{k}{k-1} RT\left[\left(\frac{p_0}{p}\right)^{\frac{k-1}{k}} - 1\right].$$

---

[1] Further the line above k is omitted.

Then from Bernoulli equation when $L_т = 0$ and with adiabatic process

$$\frac{p_0}{p} = \left[1 + \frac{k-1}{2} M^2 - g(k-1)\frac{Q_{диссип}}{a^2}\right]^{\frac{k}{k-1}}. \qquad (II.89)$$

As can be seen from this equation, dissipation of energies leads to lowering of stagnation pressure. Therefore, in spite of isolation of working medium from the environment with adiabatic stagnation, the total stagnation pressure along the flow path will always drop, since due to internal friction the mechanical form of motion changes into thermal and causes rise of entropy.

Total stagnation pressure will remain constant if we allow the absence of internal friction and constancy of entropy. In such a particularly theoretical, so-called <u>isentropic</u>, process ds = 0, $dp_0 = 0$ and stagnation pressure will be determined so:

$$\frac{p_{0из}}{p} = \left(1 + \frac{k_{из}-1}{2} M^2\right)^{\frac{k_{из}}{k_{из}-1}}. \qquad (II.90)$$

Here index "из" indicates the difference of adiabatic and isentropic processes.

Formula (II.90) can be obtained directly from expression (II.87) for stagnation temperature. For this let us use proportions from equation of process (II.74):

$$\frac{p_0}{p} = \left(\frac{T_0}{T}\right)^{\frac{k}{k-1}} \qquad (II.91)$$

and

$$\frac{\rho_0}{\rho} = \left(\frac{T_0}{T}\right)^{\frac{1}{k-1}}. \qquad (II.92)$$

On the basis of (II.92) from (II.87) there is obtained a formula for calculating the density in isentropically stagnated flow

$$\frac{\rho_{0из}}{\rho} = \left(1 + \frac{k-1}{2} M^2\right)^{\frac{1}{k-1}}. \qquad (II.93)$$

Equation of state (II.51) is extended to stagnated parameters

$$p_0 = g\rho_0 R T_0. \tag{II.94}$$

In adiabatic and isentropic flows the stagnation temperature T_0 serves for appraisal of overall energy of all forms of motions, and stagnation pressure p_0 for appraisal of mechanical motion.

§ 12. Acceleration of Gas Flows and Transformation of Energy

For obtaining the greatest value of reactive force in liquid-propellant rocket engines it is necessary to carry out the most complete conversion of internal energy of working medium and energy from intermediate external sources into kinetic energy of the outflowing gas stream. Therefore, acceleration of gas flows is a central problem in organizing the processes of conversion of forms of motions participating in gas flows.

Generally by equation of conservation of energy (II.64)

$$d\left(\frac{w^2}{2g}\right) = dQ_{\text{внеш}} - dL_{\text{т}} - dI$$

The change of kinetic energy along the flow path (acceleration of gas) can be attained by:

a) supply of heat $dQ_{\text{внеш}}$ externally, from an intermediate source;

b) imparting mechanical work $dL_{\text{т}}$ from an external (intermediate) machine;

c) decrease of enthalpy of working medium dI.

In basic types of liquid-propellant rocket engine propulsion systems, operating by the use of internal chemical energy of propellant, acceleration of gas is accomplished by decrease of enthalpy of working medium.

On the basis of equation of conservation of energy the rational method of acceleration of gas flows should consist of the fact that the total result during conversions of different types of energy would be made up from transition of each form of motion ($dQ_{\text{внеш}}$, dL and dI) into kinetic energy, as is illustrated on the transformation diagram on Fig. II.7a and b.

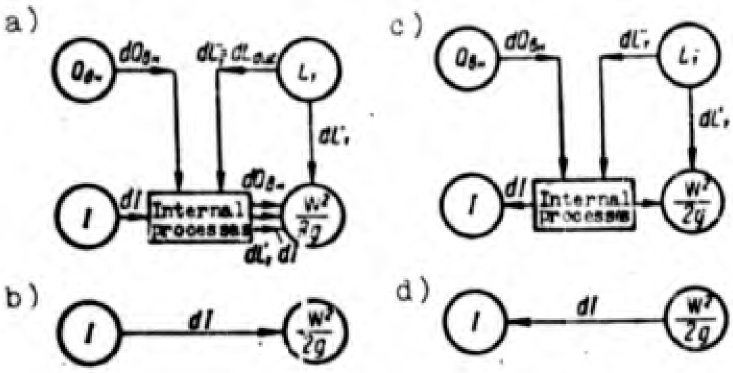

Fig. II.7. Diagrams of transformation of energy during acceleration of gas flows.

The case of transformation of energy, shown on Fig. II.7c, is not rational, since rise of enthalpy along the path of the process decreases the possible acceleration of gas. The case on Fig. II.7d characterizes stagnation of flow.

Thus, from the point of view of rational transformation of energy the decrease of enthalpy of working medium along the path of motion should be a necessary condition.

$$dI < 0. \tag{II.95}$$

For gas on the basis of (II.26) this condition

$$dI = c_p dT$$

can be interpreted so:

$$dT < 0. \tag{II.96}$$

which signifies the necessity of lowering the temperature of gas along the path of motion.

Proceeding from equation of state (II.48)

$$pv = NR_{\mu}T$$

condition (II.96) for reacting gas can be written in the form

$$R_{\mu}dT = d\left(\frac{pv}{N}\right) = \frac{dp}{p} + \frac{dv}{v} - \frac{dN}{N} < 0. \qquad \text{(II.97)}$$

In polytropic equation (II.74) in differential form

$$\frac{dp}{p} + n\frac{dv}{v} = 0$$

it is possible to replace $\frac{dp}{p}$ so:

$$\frac{dp}{p} = -n\frac{dv}{v}.$$

Then condition (II.97) will be rewritten in the following way:

$$\left(1 - n - \frac{v}{N}\frac{dN}{dv}\right)\frac{dv}{v} < 0. \qquad \text{(II.98)}$$

This condition is satisfied in processes of gas expansion when $dv>0$, when there will be satisfied inequality

$$\left(-n + 1 - \frac{v}{N}\frac{dN}{dv}\right) < 0,$$

which is observed in case

$$n > \left(1 - \frac{v}{N}\frac{dN}{dv}\right). \qquad \text{(II.99)}$$

It is not difficult to note that expression $\left(1 - \frac{v}{N}\frac{dN}{dv}\right)$ represents the value of index of process n_i at constant value of enthalpy of reacting gas:

$$n_{i=\mathrm{const}} = 1 - \frac{v}{N}\frac{dN}{dv} = 1 - \frac{v}{N}\frac{dN/dT}{dv/dT}. \qquad \text{(II.100)}$$

However, inequality (II.99) should be still supplemented by an upper limit, so that n would not be greater than $k_{\text{нз}}$, since $n>k_{\text{нз}}$ would signify not the addition of external heat for increasing kinetic energy of working medium, but removal of heat from the working medium. Therefore, condition of rational transformation of energy with use of external heat and external work for acceleration of gas will be written in the form

$$k_{\text{нз}} > n > n_1. \tag{II.101}$$

In nonreacting gas (dN = 0) this will look so:

$$k_{\text{нз}} > n > 1.$$

Thus, acceleration of gas flows should be accomplished by gas expansion. Region of rational expansion processes in accordance with condition (II.101) is shown in Fig. II.8.

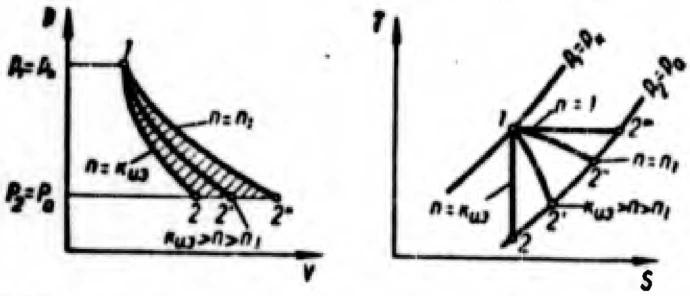

Fig. II.8. Image of expansion processes during acceleration of flow in reacting gases.

Ranges of possible expansions of working medium under liquid-propellant rocket engine conditions are determined by the difference between maximum pressure in combustion chamber $p_{\text{к}}$ and pressure p_a at nozzle box exit in its outermost section. By these pressure ranges there are determined the quantities of different types of energy, which are converted into kinetic energy of the stream.

On Fig. II.8 the initial states of working medium, corresponding to maximum pressure, are designated by point 1.

Isentropic process of expansion in the assigned range of pressure change from $p_1 = p_к$ to $p_2 = p_a$ is represented by curve 1-2.

With the addition of heat and the presence of energy dissipation according to equation (II.60)

$$ds = \frac{dQ_{\text{внеш}} + dQ_{\text{диссип}}}{T}$$

there always occurs rise of entropy, therefore such processes on diagram T-s of Figs. II.8 and II.9 are arranged on the right of isentropic process.

Figure II.9 shows graphic characteristics of quantitative transformations of separate forms of energy.

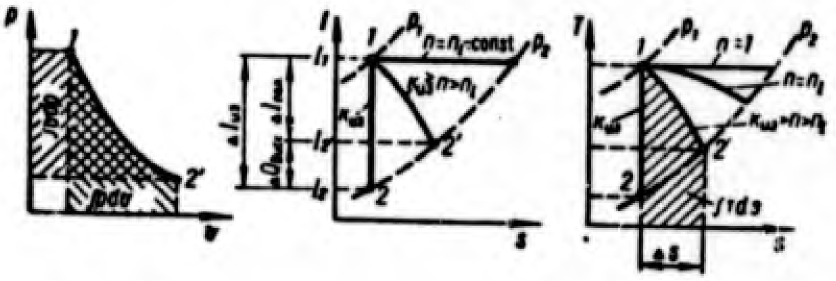

Fig. II.9. Graphic representation of quantitative transformations of separate forms of energy.

The most use of enthalpy of working medium $\Delta I_{\text{из}}$, with expansion in organic range of pressures from p_1 to p_2, according to diagram I-s of Fig. II.9 is possible at ideal isentropic process 1-2, i.e., when external heat and external mechanical work ($dQ_{\text{вн}}$ and $dL_{\text{т}}$) do not take part in acceleration of gas, and heat of dissipation is equal to zero. Such theoretical process would be the most advantageous for liquid-propellant rocket engines operating with the use of only internal (basically chemical) energy of propellant.

As compared to ideal isentropic expansion in polytropic processes with index $n < n_{\text{из}}$ the degree of utilization of enthalpy of working medium is decreased. The difference in changes of enthalpy $\Delta I_{\text{из}} - \Delta I_{\text{пол}}$

on diagram I-s makes up dissipation energy

$$\Delta Q_{\text{диссип}} = \Delta I_{\text{из}} - \Delta I_{\text{под}}. \qquad \text{(II.102)}$$

In the absence of $\Delta Q_{\text{внеш}}$ and $\Delta L_{\text{т}}$ the dissipation energy will be minimum.

Total effect of limiting process $n = n_1$ is characterized by the fact that $\Delta Q_{\text{внеш}}$ and $\Delta L_{\text{т}}$ are completely turned into kinetic energy of stream, and dissipation heat $\Delta Q_{\text{диссип}}$ becomes numerically equal to ΔI and, thus, enthalpy of working medium turns out to be as if excluded from creation of the effect of gas acceleration.

Interpretation of graphic characteristics of quantitative transformations of separate forms of energy during acceleration of gas flows is given in the following table.

Graphic characteristic	Polytropic process of acceleration of gas flow at $Q_{\text{внеш}} \neq 0$ and feed $L_{\text{т}}$	Adiabatic isolated process with energy dissipation	Ideal isentropic process $Q_{\text{диссип}} = 0$
$-\int v\,dp$	$(I_1 - I_2) + Q_{\text{внеш}} + Q_{\text{диссип}}$ $\frac{w_2^2 - w_1^2}{2g} - L_{\text{т}} + Q_{\text{диссип}}$	$(I_1 - I_2) + Q_{\text{диссип}}$ $\frac{w_2^2 - w_1^2}{2g} + Q_{\text{диссип}}$	$I_1 - I_2$ $\frac{w_2^2 - w_1^2}{2g}$
$\int p\,dv$	$(U_1 - U_2) + Q_{\text{внеш}} + Q_{\text{диссип}}$	$(U_1 - U_2) + Q_{\text{диссип}}$	$U_1 - U_2$
$\int T\,ds$	$Q_{\text{внеш}} + Q_{\text{диссип}}$	$Q_{\text{диссип}}$	0

For propulsion systems of liquid-propellant rocket engines, operating with the use of basically chemical energy of propellant, of the examined rational processes the adiabatic process with inevitable energy dissipation will be the most optimum. Ideal isentropic process attracts simplicity of calculation formulas and can be considered as the limiting theoretical case for comparative appraisal of the degree of perfection of real processes.

If we assume that all other available forms of energy ($I_{\text{нач}}$, $Q_{\text{внеш}}$ and $L_{\text{т}}$), are converted into kinetic energy of gas stream, then the velocity of gas, corresponding to this kinetic energy, is called ideal theoretical. By equation of conservation of energy, written for 1 kg of working medium, we will obtain

$$w_{\text{ид}}=\sqrt{2g\left(I_{\text{нач}}+Q_{\text{внеш}}-L_{\text{т}}\right)+w_1^2}. \qquad \text{(II.103)}$$

Here all forms of energy are represented in dimensionality kg·m;

W_1 – initial velocity of working medium with respect to coordinates, connected with channel walls.

In case $Q_{\text{внеш}}=0$ and $L_{\text{т}}=0$ ideal theoretical velocity $w_{\text{ид}}$ depends only on initial enthalpy of working medium $I_{\text{нач}}$, i.e., on enthalpy of propellant. During calculations of acceleration of gaseous combustion products as $I_{\text{нач}}$ there is considered enthalpy of these products in the combustion chamber $I_{\text{пр.сг}}$ at chamber temperature $T_{\text{к}}$:

$$w_{\text{ид}}=\sqrt{2gI_{\text{нач}}+w_1^2}.$$

Taking into account (II.86)

$$I_{\text{нач}}=\int c_p\,dT=\bar{c}_pT_{\text{к}}=\frac{\bar{k}}{\bar{k}-1}RT_{\text{к}}$$

we will obtain

$$w_{\text{ид}}=\sqrt{\frac{2g\,427\,\bar{k}}{\bar{k}-1}RT_{\text{к}}}=91{,}53\sqrt{\frac{\bar{k}}{\bar{k}-1}RT_{\text{к}}} \qquad \text{(II.104)}$$

when $w_1=0$.

During analysis of equation of type (II.104) it is necessary to proceed from the fact that $w_{\text{из}}$ is determined only by reserve of initial energy $I_{\text{нач}}$, and one should not pay attention to the influence of separate physical properties of working medium entering the formula ($\overline{k}$, R or $\overline{c}_p$), since they appear in the complex.

§ 13. Calculated Theoretical Exhaust Velocity and Thermal Efficiency

It is impossible to entirely convert all available thermal energy, chemical energy and external mechanical work into directed kinetic energy of gas stream. This is prevented by two basic reasons:

1) dissipation of energy, connected with irreversibility of processes, which is expressed in the fact that along the flow path part of the kinetic energy will be converted back into heat;

2) limitation of expansion range between maximum permissible pressure in combustion chamber $p_1 = p_\text{к}$ and finite quantity of pressure $p_2 = p_a$ in nozzle box exit section. Therefore, even in energetically isolated flow the working medium always possesses some connected part (thermal or chemical) of energy, which turns out to be not converted into kinetic directed energy of stream.

Ratio of obtained rise of kinetic energy of stream to all the converted energy is called thermal efficiency.

According to equation of conservation (II.64) the rise of kinetic energy

$$\frac{w_2^2 - w_1^2}{2g} = Q_{\text{внеш}} - L_\text{т} + (I_1 - I_2).$$

From this formula we obtain the equation for calculated theoretical exhaust velocity in the form

$$w_a = \sqrt{2g\,[(I_1 - I_2) + Q_{\text{внеш}} - L_\text{т}] + w_1^2}\,. \qquad \text{(II.105)}$$

and in adiabatically isolated processes

$$w_a = 91{,}53\sqrt{I_1 - I_2} \quad \text{or} \quad w_1 = 0. \tag{II.106}$$

Thermal efficiency

$$\eta_t = \frac{(I_1 + Q_{\text{внеш}} - L_т) - I_2}{(I_1 + Q_{\text{внеш}} - L_т)} = 1 - \frac{I_2}{I_1 + Q_{\text{внеш}} - L_т}, \tag{II.107}$$

and in adiabatically isolated flows

$$\eta_t = 1 - \frac{I_2}{I_1} = 1 - \frac{\bar{c}_{p_2} T_2}{\bar{c}_{p_1} T_1}. \tag{II.108}$$

Calculated theoretical exhaust velocity, taking thermal efficiency into account will be written so:

$$w_a = \sqrt{2g(I_1 + Q_{\text{внеш}} - L_т)\eta_t + w_1^2} \tag{II.109}$$

and for adiabatic acceleration of flow at initial velocity $w_1 = 0$ we will obtain

$$w_a = 91{,}53\sqrt{I_1 - I_2} = 91{,}53\sqrt{I_1 \eta_t}, \tag{II.110}$$

where I is in kcal/kg.

If we assume $\bar{c}_{p_2} \approx \bar{c}_{p_1}$ and express the temperature ratio according to equation of polytropic process through the pressure ratio, then instead of (II.106) and II.108) it is possible to write

$$\eta_t = 1 - \left(\frac{p_2}{p_1}\right)^{\frac{n-1}{n}}; \tag{II.111}$$

$$w_a = \sqrt{2g\frac{\bar{k}}{\bar{k}-1}RT_к\left[1 - \left(\frac{p_2}{p_1}\right)^{\frac{n-1}{n}}\right]}. \tag{II.112}$$

Equations (II.111) and (II.112) are less exact than (II.106) and (II.108), whereas they are identical in outline to analogous equations for ideal nonreacting gases, and therefore they are often used during therodynamic calculations.

§ 14. Analysis of Formula for Thermal Efficiency

One of the main factors of increase of thermal efficiency during acceleration of gas flows in liquid-propellant rocket engines is the expansion of the pressure range in which there is carried out conversion of energy. This ratio is usually assigned pressure ratio $\frac{p_2}{p_1}$, which is called the expansion ratio. We distinguish:

possible expansion ratio δ, which is determined by ratio of counterpressure of environment p_H in which outflow of gases from the nozzle occurs, to maximum pressure in the combustion chamber p_K by formula

$$\delta = \frac{p_H}{p_K}; \qquad \text{(II.113)}$$

geometric expansion ratio π, being the ratio of calculated pressure in nozzle exit section p_a to pressure before the nozzle

$$\pi = \frac{p_a}{p_K}. \qquad \text{(II.114)}$$

In calculated operating mode of nozzle box

$$\pi = \delta; \quad p_a = p_H, \qquad \text{(II.115)}$$

i.e., the nozzle is designed in such a manner that in the exit section pressure p_a is equal to counterpressure of environment p_H.

Usually the effect of expansion ratio $\frac{p_2}{p_1}$ on thermal efficiency is examined at calculated nozzle operating conditions. This effect is manifested through external conditions p_H and calculated pressure p_K before the nozzle (in combustion chamber).

In adiabatically isolated ideal isentropic flows the change of $\eta_t = f(\delta)$ according to equation (II.111) at various, but constant values of index $\kappa_{из}$ is shown on Fig. II.10.

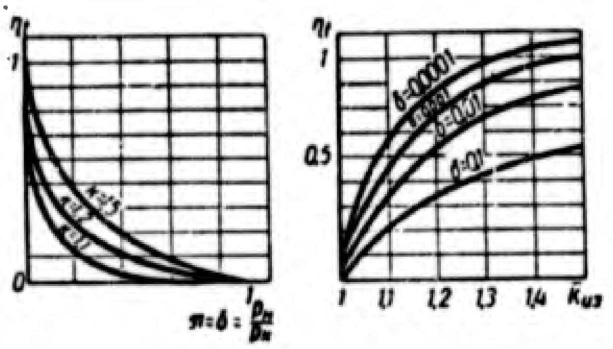

Fig. II.10. Effect of expansion ratio and index of isentropic process on thermal efficiency.

From this figure it is clear that with tendency $p_a \to 0$ (in vacuum) or with infinite pressure increase in chamber $p_k \to \infty$ the thermal efficiency in isentropic ideal flow approaches one, and exit velocity – to ideal theoretical velocity.

At assigned expansion ratio $\pi = \delta$ the thermal efficiency turns out to be connected with the type of working medium through index of process $k_{из}$.

According to equation (II.35)

$$\bar{k}_{из} = 1 - \frac{1.985}{\bar{c}_v}$$

index $\bar{k}_{из}$ will depend on heat capacities of gases $\bar{c}_v$, making up the combustion products.

Thermal efficiency increases with increase of $\bar{k}_{из}$. The largest value of $\bar{k}_{из} = 1.67$ can occur for nonreacting monatomic gases. With increase of atomicity of individual nonreacting gases, their heat capacity c_v increases, and index $\bar{k}_{из}$ is decreased.

In the mixture of reacting gases $\bar{k}_{из}$ is greater, the larger the content of monatomic and low-atomic gases in this mixture. Therefore, from the point of view of obtaining the most efficiency at the same chemical energy reserve, the propellant, toplibo, in the composition of combustion products of which there is contained more low-atomic gases, will be the best.

In chemically reacting gases according to exact formula (II.34)

$$k=\frac{c_p}{c_v}=\frac{\bar{c}_p+\sum I_i\left(\frac{\partial N_i}{\partial T}\right)_p}{\bar{c}_v+\sum U_i\left(\frac{\partial N_i}{\partial T}\right)_v}$$

index $k_{\text{из}}$ will be smaller than approximate value of $\bar{k}_{\text{из}}$, since $\sum I_i\left(\frac{\partial N_i}{\partial T}\right)_p$ and $\sum U_i\left(\frac{\partial N_i}{\partial T}\right)_v$ are always positive and

$$\left(\frac{\partial N_i}{\partial T}\right)_p>\left(\frac{\partial N_i}{\partial T}\right)_v.$$

As can be seen from Fig. II.10, the effect of index $k_{\text{из}}$ and expansion ratio δ on thermal efficiency in ideal isentropic process appears the most noticeably at small values of $k_{\text{из}}$ (approaching one) and δ (approaching zero).

Thus, in the ideal isentropic process of expansion thermal efficiency is continuously increased with decrease of expansion ratio δ, approaching one. This leads to the conclusion that with infinitely large expansion the thermal efficiency becomes equal to one.

However, such a conclusion will be incorrect as soon as we try to consider nonisentropy of processes in relation to cause of energy dissipation and friction on walls.

On the basis of (II.58) and (II.60) with unlimited expansion of pressures limits in the nozzle box the work of dissipative forces will approach maximum value, at which all kinetic energy of directed motion will change into the form of thermal energy and thermal efficiency will become equal to zero.

Such a picture is depicted on Fig. II.11, where dotted lines show change of η_t from pressure ratio $\frac{p_1}{p_2} = \frac{p_k}{p_a}$ at ideal isentropic acceleration of gas flows, and solid lines represent change of η_t at adiabatically isolated flow taking into account dissipation of energy (curve a), at additional calculation of friction against nozzle walls (curve b) and at possible chemical nonequilibrium (curve c).

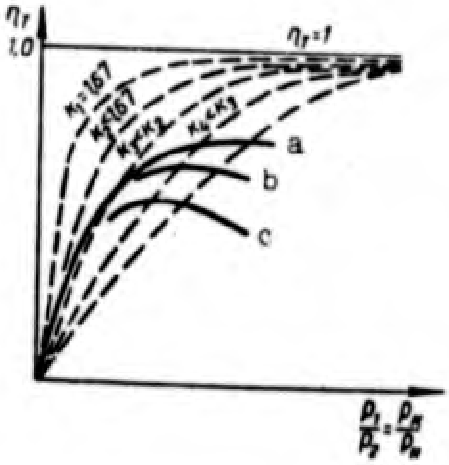

Fig. II.11. Approximate change of thermal efficiency during adiabatically isolated expansion taking into account energy dissipation and friction against walls: (a) taking into account energy dissipation; (b) with additional calculation of friction against walls; (c) with possible irregularity.

Thus, in contrast to ideal isentropic expansion during adiabatica adiabatically isolated flow taking into account the dissipation of energy, theoretical values of thermal efficiency with increase of ratio $\frac{p_k}{p_a}$ should pass through maximum.

Friction against channel walls and possible chemical nonequilibrium of processes lower maximum value of efficiency and displace the point of maximum toward smaller ratios $\frac{p_k}{p_a}$.

Degree of energy dissipation depends not only on pressure ratio limits, but also on the design and manufacture of nozzle box.

As a limiting case there can be considered the process of so-called gas throttling through the throttle device, when with lowering of pressure from p_1 to p_2 the enthalpy is not changed $I_1 = I_2$ and thermal efficiency becomes equal to zero at all values of p_1/p_2.

Designing of propulsion systems, operating at ground conditions (with $p_н$ close to one), with calculation for higher pressures in the combustion chamber, permits increasing the thermal efficiency to maximum theoretical value. In existing liquid-propellant rocket engines with increase of $p_к$ at ground conditions even to 300 atmospheres $\left(\delta = \frac{p_н}{p_к} > 0{,}003\right)$ the maximum of efficiency is apparently still not attained.

However, propulsion systems of liquid-propellant rocket engines, operating at high altitudes (with $p_н$ less than 0.1 atm) and in a vacuum, should be designed with a view toward such pressures in the combustion chamber, in order not to cross through the point of maximum efficiency.

CHAPTER III

LIQUID-PROPELLANT ROCKET ENGINE THRUST

The basic assignment of a liquid-propellant rocket engine is the creation of thrust P in a definite time interval t.

For example, each rocket has its own program of change of thrust along the rocket flight path, making it possible at minimum rocket weight to reach the prescribed terminal velocity, which, for example, determines the flight range for ballistic missiles.

Without exact knowledge of the thrust value and its dependence on some parameters it is impossible to design a rocket with optimum characteristics. First let us determine thrust created by the combustion of a liquid-propellant rocket engine, which is simultaneously the thrust of a liquid-propellant rocket engine in a case when discharge of combustion products of propellant into the environment occurs only through the combustion chamber (liquid-propellant rocket engine with pressurized fuel feed, liquid-propellant rocket engine with turbopump fuel feed system, operating on a closed system, etc.). Case of calculation of liquid-propellant rocket engine thrust, when part of the propellant is expended on generation of working medium for the turbine with its subsequent discharge into the environment, will be considered at the end of the section.

Combustion chamber thrust is resultant force, created due to the action of pressure forces of working medium on the internal surface and forces of ambient pressure on the external surface of combustion chamber and nozzles, which together fulfill the role of propelling agent.

On Fig. III.1 it is clear that the internal surface of combustion chamber is affected by variable pressure, which is changed from pressure in combustion chamber $p_к$ to pressure on nozzle section p_c.

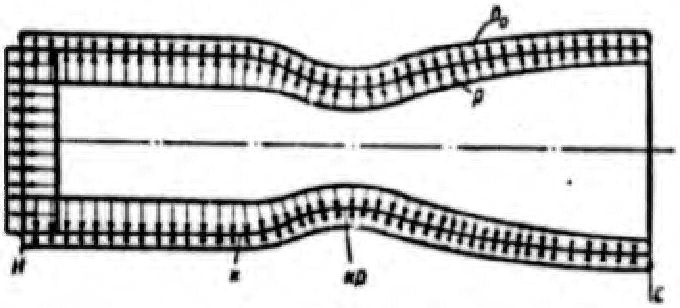

Fig. III.1. Forces affecting walls of combustion chamber of cylindrical shape.

The external surface of chamber is affected by constant ambient pressure p_0.

Combustion chamber thrust can be determined as resultant pressure forces, affecting the internal and external surface of the combustion chamber, or with the help of equation of momentum. Both methods are widely used for calculating combustion chamber thrust and have their characteristic advantages and disadvantages. Since the first method permits deeply penetrating the physical essence of the nature of thrust, determining the portion of thrust obtained from separate parts of the combustion chamber and place of their application, and estimating the degree of perfection of separate elements of the chamber, the second method permits rapidly determining combustion chamber thrust, but does not reveal the mechanism and nature of gas-dynamic phenomena occurring inside the combustion chamber. Therefore, below there will be given derivation of thrust formula by both methods.

During formulation of thrust equation let us take motion of gases as steady and one-dimensional. Propellant combustion products, which are recombined during flow in nozzle, are replaced by ideal gas, for which constant mean values of outflow index k and gas constant are selected in such a way that the geometry of nozzle and gas flow velocity are identical to geometry of nozzle and exit velocity of real combustion products.

Friction and heat exchange between gas and combustion chamber walls will be disregarded.

§ 1. Determination of Thrust as Resultant Pressure Forces

With derivation of thrust formula let us take a combustion chamber of arbitrary shape (Fig. III.2), and nozzle section pressure as generally occurs, different from ambient pressure.

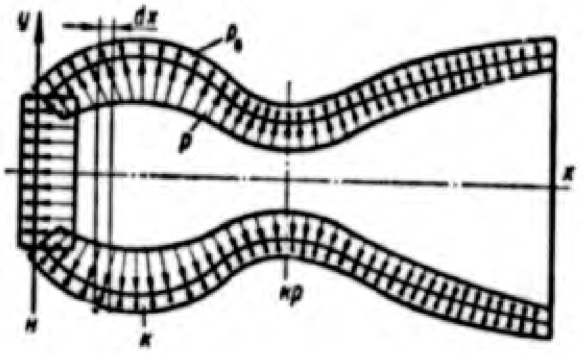

Fig. III.2. Forces affecting walls of combustion chamber of arbitrary shape.

According to determination combustion chamber thrust

$$P = \int_s p \cos\left(\widehat{n\, x}\right) ds. \qquad \text{(III.1)}$$

where n – normal to the surface; x – axis of chamber; s – total (internal and external) surface of chamber.

For solution of this integral let us divide thrust into four components, while components of thrusts, coinciding in direction with outflow velocity vector, will be taken positive and conversely

$$-P = -P_1 - P_2 + P_3 - P_4. \qquad \text{(III.2)}$$

where P_1, P_2, P_3, P_4 – resultant pressure forces affecting the chamber head, the divergent section of the chamber, the contraction section of the combustion chamber (including the subcritical part of the nozzle) and the supercritical part of the nozzle.

With determination of resultant pressure forces on the chamber head we will consider that all the propellant reserve is in the chamber head, where, as in the tank, the velocity of liquid is negligible.

Similar assumption does not affect the final results of derivation, and computations are simplified. For determination of force P_1 let us use the theorem of momentum for the volume of liquid enclosed in the head cavity. For this let us limit the head by control surface and apply external forces, affecting the separated contour for liquid (Fig. III.3).

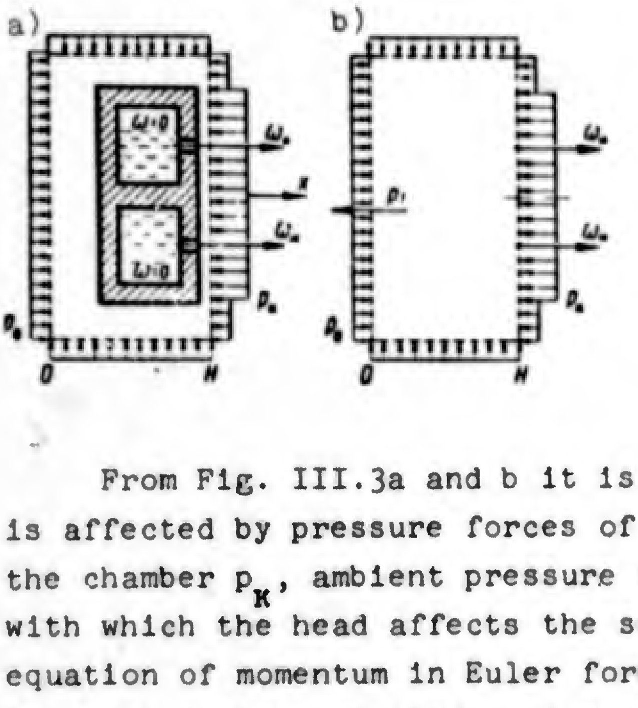

Fig. III.3. Calculated diagram for determining force P_1.

From Fig. III.3a and b it is clear that the separated contour is affected by pressure forces of gases in the initial section of the chamber $p_к$, ambient pressure forces p_0 and unknown force P_1, with which the head affects the separated contour. According to equation of momentum in Euler form the sum of projections of all external forces, applied to the examined contour of liquid, to axis x is equal to projection of the change of momentum per second:

$$P_x = \frac{G}{g}(W_{x_2} - W_{x_1}). \qquad \text{(III.3)}$$

where W_{x_1} and W_{x_2} – axial components of liquid velocity at the entrance and exit of the separated contour.

In our case $W_{x_1} = 0$, and $W_{x_2} = W_H$, then

$$P_x = \frac{G}{g} W_H. \tag{III.4}$$

At the same time, projection of all external forces, affecting the separated contour, i.e., force P_x, equals

$$P_x = -P_1 - F_H(p_H - p_0), \tag{III.5}$$

where F_H – area of initial section of combustion chamber.

All radial components of pressure forces, affecting the walls of combustion chamber, in view of the chamber's axisymmetry are mutually balanced. Axial components of pressure forces, which in the sum give unknown force $-P_1$, remain unbalanced. The "minus" sign for force P_1 means that it is directed to the side opposite the positive direction of axis x. Further, all forces coinciding in direction with axis x, will be considered positive, and conversely.

With the help of equation (III.5), substituting the value of P_x from equation (III.4), we will obtain the value of force P_1:

$$-P_1 = \frac{G}{g} W_H + F_H(p_H - p_0). \tag{III.6}$$

For determination of force P_2 (Fig. III.4a) let us sum axial components of pressure forces affecting the divergent section of combustion chamber between sections H and K.

Axial projection of pressure forces affecting the annular element of combustion chamber with width dx:

$$-dP_2 = (p - p_0)\, ds \cos\alpha,$$

where ds – surface of elementary cone with height dx; α – angle between positive direction of axis x and the normal to the surface.

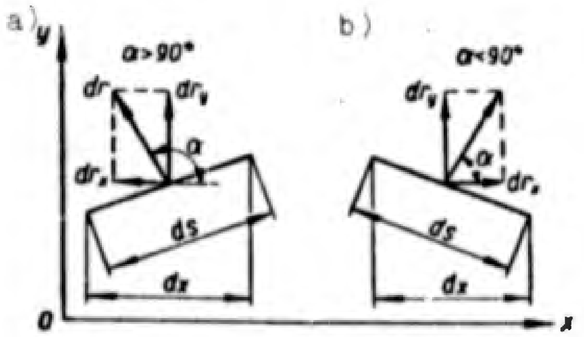

Fig. III.4. Calculated diagram for determining forces P_2 and P_3.

Considering that ds cos α is a projection of area ds to the plane perpendicular to the axis, force

$$-dP_2 = (p - p_0)\,dF,$$

where

$$dF = ds\cos\alpha.$$

By integrating the last equation by the entire surface of the considered chamber section, we will obtain

$$-P_2 = \int_{F_н}^{F_к} (p - p_0)\,dF = \int_{F_н}^{F_к} p\,dF - p_0(F_к - F_н).$$

By integrating p dF by parts we find that

$$\int_{F_н}^{F_к} p\,dF = p_к F_к - p_н F_н - \int_{p_н}^{p_к} F\,dp.$$

By using continuity and Bernoulli equations

$$F = \frac{G}{gW}; \quad W\,dW = -\frac{dp}{\rho},$$

and also considering that during steady state engine operation G = const, we obtain

$$\int_{F_н}^{F_к} p\,dF = p_к F_к - p_н F_н + \int_{W_н}^{W_к} \frac{G\gamma}{W\gamma g} W\,dW =$$

$$= p_к F_к - p_н F_н + \frac{G}{g}(W_к - W_н).$$

Let us place the value of integral $\int\limits_{F_н}^{F_к} pdF$ in the equation for force P_2, then

$$-P_2 = p_к F_к - p_н F_н + \frac{G}{g}(W_к - W_н) - \bar{p}_0(F_к - K_н). \qquad \text{(III.7)}$$

Forces P_3 (Fig. III.4b) and P_4 (Fig. III.4a) are obtained analogously:

$$P_3 = \int\limits_{F_к}^{F_{кр}} (p - p_0)\,dF = p_{кр}F_{кр} - p_к F_к + \frac{G}{g}(W_{кр} - W_к) - p_0(F_{кр} - F_к); \qquad \text{(III.8)}$$

$$-P_4 = \int\limits_{F_{кр}}^{F_c} (p - p_0)\,dF = p_c F_c - p_{кр} F_{кр} + \frac{G}{g}(W_c - W_{кр}) -$$
$$- p_0 (F_c - F_{кр}). \qquad \text{(III.9)}$$

By substituting forces P_1, P_2, P_3 and P_4 with their sign in equation (III.2), we obtain the final formula for calculating thrust force of the combustion chamber

$$-P = \frac{G}{g} W_c + F_c (p_c - p_0). \qquad \text{(III.10)}$$

In the practice of engine manufacture cylindrical combustion chambers, for which force $P_2 = 0$ (see Fig. III.1) received wide propagation. It is interesting to note that thrust formula (III.10) is not changed with this. Actually, thrust of cylindrical-shaped combustion chamber

$$-P = -P_1 + P_3 - P_4 = \frac{G}{g} W_c + F_c (p_c - p_0) -$$
$$- \frac{G}{g}(W_к - W_н) + F_к (p_н - p_к).$$

Considering that with gas motion along a cylindrical pipe there is valid relationship

$$F_к (p_н - p_к) = \frac{G}{g}(W_к - W_н).$$

we will obtain the same expression (III.10) for thrust of a cylindrical-shaped combustion chamber. Thus, combustion chamber thrust from a gas-dynamic point of view does not depend on its shape.

§ 2. Derivation of Thrust Formula from Momentum Equation

Formula (III.10) can be obtained directly from momentum equation (III.3). In this case there is no need of detailed consideration of pressure forces affecting the walls of combustion chamber, it is necessary to know only the pressure, velocity and flow rate per second of gas at control surface entry and exit.

Let us draw the control surface near the combustion chamber, so that one of its planes passes along the nozzle section, where all the shown parameters are known, let us draw the other sides of control surface arbitrarily, but in such a manner that the combustion chamber is inside the control surface. Diagram of external forces, applied to the contour, is presented on Fig. III.5. As earlier, let us write projections to the axis of external forces, applied to the separated contour:

$$P_x = -P - F_c(p_c - p_0).$$

According to momentum equation

$$-P = \frac{G}{g} W_c + F_c(p_c - p_0),$$

i.e., we obtained unknown thrust formula (III.10). Usually in practice we are concerned with the absolute value of thrust and the

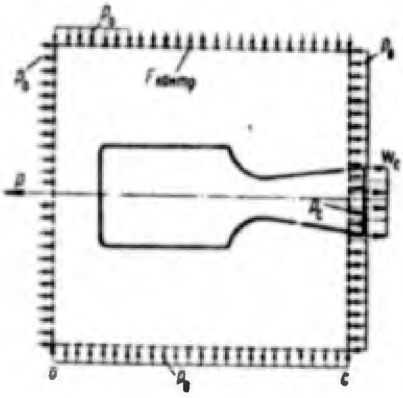

Fig. III.5. Calculated diagram for determination of thrust by theorem of momentum.

"minus" sign is omitted, and thrust formula is written in the form

$$P=\frac{G}{g}W_{c}+F_{c}(p_{c}-p_{0}). \qquad \text{(III.11)}$$

§ 3. Analysis of Thrust Formula

Formula of combustion chamber thrust was obtained by summation of pressure forces affecting the internal and external surface of the combustion chamber:

$$P=\int\limits_{s} p\,ds\cos\left(\widehat{n\,x}\right)=\frac{G}{g}W_{c}+p_{c}F_{c}-p_{н}F_{c}.$$

This integral can be split into two

$$P=\int\limits_{s_{\text{внутр}}} p\,ds\cos\left(\widehat{n\,x}\right)-\int\limits_{s_{\text{внеш}}} p_{0}\,ds\cos\left(\widehat{n\,x}\right), \qquad \text{(III.12)}$$

of which the first characterizes thrust, created due to pressure forces applied to the internal contour of combustion chamber, and the second - thrust, which is created due to ambient pressure forces applied to the external contour, i.e.,

$$P_{\text{внутр}}=\int\limits_{s_{\text{внутр}}} p\,ds\cos\left(\widehat{n\,x}\right)=\frac{G}{g}W_{c}+p_{c}F_{c}, \qquad \text{(III.13)}$$

$$P_{\text{внеш}}=\int\limits_{s_{\text{внеш}}} p\,ds\cos\left(\widehat{n\,x}\right)=p_{0}F_{c}. \qquad \text{(III.14)}$$

It is necessary to clearly analyze the nature of thrust. Thrust taken from the internal contour $P_{\text{внутр}}$, depends only on working process parameters in the combustion chamber. This is reactive force. In case of nondependence of the working process in combustion chamber on ambient pressure nozzle (operating conditions without shock waves in the nozzle, caused by the influence of ambient pressure), this component characterizes thrust in a void, i.e., when $p_0 = 0$

$$P_{\text{внутр}}=P_{\text{п}}.$$

Thrust, taken from the external contour $P_{\text{внеш}}$, characterizes the influence of only external pressure. It has no relationship with jet thrust, often called dynamic thrust component. From formula (III.11) it follows that it is possible to increase thrust by increase of propellant consumption and exhaust velocity of combustion products W_c. The greatest value of thrust at prescribed combustion chamber parameters is attained when $p_0 = 0$, i.e., in a vacuum. When negative thrust component $p_0F_c = P_{внеш}$ equals zero, thrust force is determined completely by reactive force

$$P = P_{внутр} = \frac{G}{g} W_c + p_c F_c. \qquad \text{(III.15)}$$

Consequently, thrust at some ambient pressure is connected (with shock-free nozzle operating conditions) with thrust $P_{внутр}$ by relationship

$$P = P_{внутр} - p_0 F_c. \qquad \text{(III.16)}$$

It is necessary to pause on one more concept — rated operating conditions of combustion chamber nozzle. These are conditions at which pressure on the nozzle section is equal to ambient pressure. In this case thrust formula

$$P_{расч} = \frac{G}{g} W_c. \qquad \text{(III.17)}$$

Operating conditions of combustion chamber nozzle have a great influence on the value of thrust. Naturally it is necessary to know at what nozzle operating conditions the combustion chamber will develop the greatest thrust. With the prescribed pressure in combustion chamber it is possible to designate various expansion ratios of gases in the nozzle, at which pressure on the nozzle section can be greater, less and equal to ambient pressure. With prescribed pressure in the combustion chamber it is necessary for us to select such an expansion ratio (i.e., determine pressure on nozzle section), at which the combustion chamber will develop the greatest thrust. From thrust equation (III.11) one cannot immediately see at what expansion ratio (when p_0 = const, $p_к$ = const, G = const) there is attained maximum value of combustion chamber thrust. Actually, with increase of expansion ratio when $p_к$ = const the exit velocity

$$W_c = \sqrt{2g\frac{k}{k-1}RT_k\left[1-\left(\frac{p_c}{p_k}\right)^{\frac{k-1}{k}}\right]}$$

will increase, but with this the second term $F_c(p_c - p_0)$ is decreased, becomes equal to zero when $p_c = p_0$ and with further increase of expansion ratio, when $p_c < p_0$, becomes negative. With decrease of expansion ratio the exit velocity W_c and term $\frac{G}{g}W_c$ in the thrust equation are decreased, and the second term $F_c(p_c - p_0)$ is increased.

It is necessary to know at what expansion ratio of gas in the nozzle or pressure on the nozzle section the value of thrust will be maximum.

Thrust equation can be converted to

$$P = \frac{G}{g}W_{\text{пр}} \qquad \text{(III.18)}$$

where $W_{\text{пр}}$ — some given exit velocity, equal to

$$W_{\text{пр}} = W_c + \frac{(p_c - p_0)F_c g}{G}. \qquad \text{(III.19)}$$

From formula (III.18) it follows that the change of thrust is determined only by behavior of the given exit velocity, since G = const. In order to establish the effect of expansion ratio (dimensionless area of nozzle $\frac{F_c}{F_{\text{кр}}}$ or p_c (p_k = const), let us differentiate equation (III.18) with respect to variable p_c and, by equating the first derivative to zero, we obtain

$$\frac{dW_{\text{пр}}}{dp_c} = \frac{dW_c}{dp_c} + \frac{1}{\rho_c W_c} - \frac{p_c - p_0}{(\rho_c W_c^2)}\,\frac{d(\rho_c W_c)}{dp_c} = 0.$$

Using the Bernoulli equation for compressible gas in differential form

$$\frac{dW_c}{dp_c} + \frac{1}{\rho_c W_c} = 0,$$

we obtain

$$\frac{dW_{np}}{dp_c} = -\frac{p_c - p_0}{(\rho_c W_c)^2} \cdot \frac{d(\rho_c W_c)}{dp_c} = 0. \qquad \text{(III.20)}$$

From equation (III.20) it is clear that function $\frac{dW_{np}}{dp_c}$ reaches extremal value when $p_0 = p_c$.

For determination of the character of extremum let us take the second derivative of $\frac{d}{dp_c}\left(\frac{dW_{np}}{dp_c}\right)$:

$$\frac{d^2 W_{np}}{dp_c^2} = -\frac{1}{\rho_c W_c} \cdot \frac{d(\rho_c W_c)}{dp_c}. \qquad \text{(III.21)}$$

From the formula it is clear that $\frac{d^2W_{np}}{dp_c^2} < 0$, since factor $\frac{1}{\rho_c W_c} > 0$ and $\frac{d(\rho_c W_c)}{dp_c}$ are also larger than zero inasmuch as in the supercritical part of the nozzle mass velocity $\rho_c W_c$ and pressure in the stream p_c are changed in one direction. Therefore, the given velocity, and consequently thrust reach maximum value when $p_c = p_0$. Similar nozzle operating conditions are called rated. Nozzle conditions when $p_c > p_0$ or $p_c < p_0$ are called partial load nozzle operating conditions. The shown derivation can be well comprehended by considering engine thrust as a result of the action of pressure forces on the external and internal surface of the chamber, from the following example.

Let us assume there are three combustion chambers, which are distinguished from each other only by pressure on the nozzle section.

Figure III.6 shows diagrams of pressure distribution of combustion products and ambient pressure, affecting the supercritical parts of the three nozzles.

Figure III.6a shows a nozzle with underexpansion of gas, i.e., $p_c > p_0$. With elongation of nozzle to dimensions, where in the nozzle exit section $p_c = p_0$ (Fig. III.6b), chamber thrust is increased by some value of $+\Delta P$, since pressure forces of combustion products, affecting the elongated part of the nozzle, are greater than forces of ambient pressure everywhere.

At conditions of overexpansion of combustion products in the nozzle ($p_c < p_0$, Fig. III.6c) the pressure of combustion products,

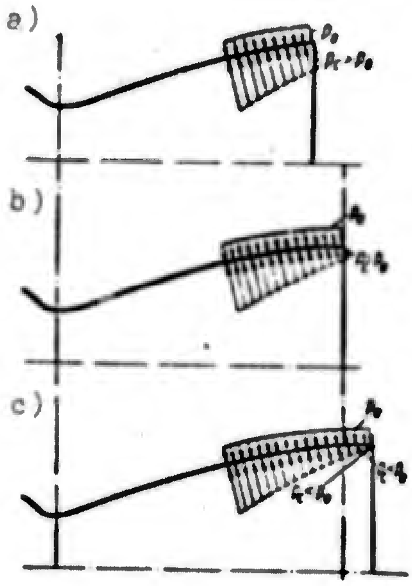

Fig. III.6. Diagram of operation of nozzle at conditions: $p_c > p_0$; $p_c = p_0$; $p_c < p_0$.

starting with the section where $p_c = p_0$, is less than ambient pressure everywhere on the wall. Therefore, projection of forces of external pressure to axis x, affecting the nozzle wall, starting with the section where $p_c = p_0$, will be larger than the projection of pressure forces affecting the same section of nozzle on the part of combustion products. As a result, this part of the nozzle gives negative thrust. Thus, both in underexpansion and overexpansion conditions the combustion chamber thrust is less than the combustion chamber thrust at rated conditions.

Consequently, for production of the greatest value of thrust for liquid-propellant rocket engines with prescribed intrachamber parameters it is necessary to design a nozzle with rated conditions of its operation. However, most liquid-propellant rocket engines operate at partial load conditions. The trajectory, for example, of long-range ballistic missiles, launched from earth, passes into a medium of variable pressure from $p_0 = 1$ [atm(abs.)] to $p_0 \ll 1$ [atm(abs.)], and pressure on the engine nozzle section is selected constant, since at present there are no designs of nozzles capable of changing their geometry and thereby maintaining rated nozzle operating conditions with a change of ambient pressure.

If we designed a nozzle with pressure on section $p_c = 1$ at, i.e., calculated for ground conditions, then the engine would develop rated thrust only at launch, i.e., at the earth's surface. Further, with ascent to altitude the chamber nozzle would operate at underexpansion conditions everywhere, and thrust of a chamber with a similar nozzle would be less as compared to a nozzle which could accomplish rated conditions at each altitude, i.e., $p_c = p_0$. If we designed a nozzle for the same engine with $p_c < 1$ [atm(abs.)], then it would operate at rated conditions at only one altitude, where ambient pressure would be equal to pressure on the nozzle section. Consequently, a nozzle with $p_c < 1$ [atm(abs.)] to the rated altitude would operate in overexpansion conditions, and after the rated altitude the nozzle would operate in underexpansion conditions. A chamber with a similar nozzle develops less thrust at all altitudes, except the rated altitude, than an engine for which it would be possible to carry out rated nozzle operating conditions at each altitude.

In connection with the above it is important to quantitatively evaluate thrust losses at various partial load nozzle operating conditions and to outline means for reducing them.

Let us consider how thrust is changed with change of dimensionless area of nozzle exit section (pressure on nozzle section) with constant pressure in chamber and environment.

Figure III.7 shows results of calculations by formulas (III.11, III.13). From Fig. III.7 it is clear that the maximum value of thrust force corresponds to rated nozzle conditions, when the geometry of the nozzle ensures expansion of gases to ambient pressure, i.e., $p_c = p_0$($f_c = 9.0$; $p_K = 60$ [atm(abs.)]; $n = 1.15$).

With decrease of dimensionless nozzle area (increase of pressure on nozzle section) by twice the thrust losses with respect to rated conditions compose 4%, and with increase of dimensionless nozzle area by twice the thrust is decreased by 0.5%. Consequently, during nozzle operation with underexpansion the thrust losses are considerably greater than during nozzle operation with overexpansion, which is easily explained if we consider combustion chamber thrust as a result of the action of pressure forces on the external and internal

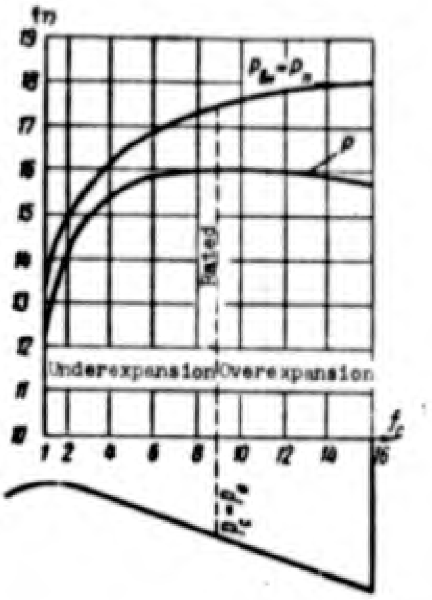

Fig. III.7. Dependence $P_0 = f(f_c$ or $p_c)$ when $p_н = \text{const}$.

surface of the combustion chamber. An important conclusion can be made if we consider the influence of pressure in the chamber on the character of thrust change with deviation of nozzle operating conditions from rated.

Figure III.8 shows change of combustion chamber thrust depending on pressure in the chamber and dimensionless nozzle area at constant ambient pressure. From Fig. III.8 it is clear that the greater the pressure in the chamber, the more smoothly thrust is changed with deviation of nozzle operating conditions from rated and conversely.

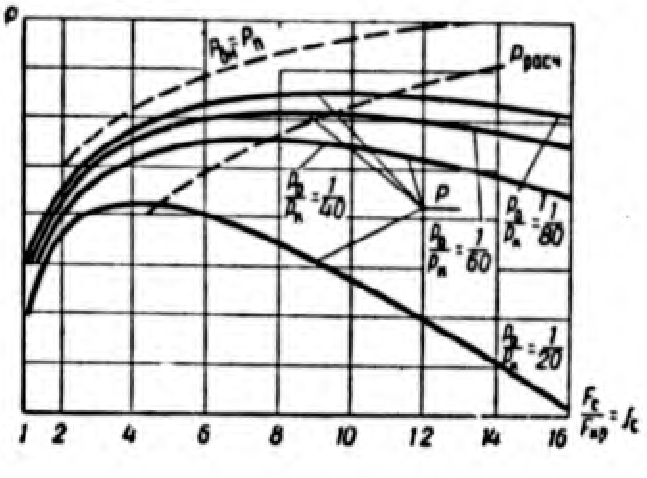

Fig. III.8. Dependence $P = f(f_c$ or $p_к)$ when $p_н = \text{const}$.

Consequently, thrust losses with deviation from rated nozzle operating conditions increase more intensively for combustion chambers with lower pressure p_K. The latter is explained by the fact that with increase of pressure in the chamber the relative ratio of thurst, obtained from the external surface of combustion chamber, to thrust, obtained from the internal surface of the chamber, is decreased. In the limit, when pressure in the chamber approaches infinity its thrust approaches that in a vacuum, i.e., the effect of static term p_0F_c will be negligible.

From Fig. III.8 one may see what a large gain in thrust the combustion chamber would give if the dimensionless nozzle area corresponded to rated nozzle conditions with change of pressure in the combustion chamber.

It is very complicated to accomplish the rated nozzle operating conditions. If for engines of rockets, whose flight path passes into medium with $p_0 > 0$ (in principle such nozzles can be created), then it is impossible to make a variable-area rated nozzle for rockets operating on the part of the trajectory with $p_0 = 0$, and all the more so for rockets for which $p_0 = 0$ along the entire flight path. Otherwise in these nozzles there should be attained an infinitely large nozzle exit section area, which is impossible.

§ 4. Specific Thrust

Specific thrust of liquid-propellant rocket engines is the name for the number of kilograms of thrust obtained from a unit of propellant consumption per second, i.e.,

$$P_{\text{уд}} = \frac{P}{G_{\text{сек}}}. \qquad \text{(III.22)}$$

At present one of the most important means of improvement of liquid-propellant rocket engines and the rocket on the whole is increase of specific thrust of the liquid-propellant rocket engine. In this section we will not elaborate on the difficulties which are before the creators of liquid-propellant rocket engines concerning increase of specific thrust. Let us consider only factors affecting specific thrust and methods of its increase.

From equation (III.11) we will obtain specific thrust, having divided the left and right sides by fuel consumption G:

$$P_{уд} = \frac{P_{внутр}}{G_{сек}} - \frac{P_{внеш}}{G_{сек}} = \left(\frac{W_c}{g} + \frac{p_c F_c}{G}\right) - \frac{p_0 F_c}{G}. \qquad (III.23)$$

From formula (III.23) it is clear that the value of specific thrust depends on parameters of the intrachamber process and ambient pressure. Specific thrust reaches maximum value at prescribed parameters of combustion chamber, as thrust, when $p_0 = 0$. Then the expression of specific thrust is fully determined by intrachamber parameters

$$P_{уд.\,внутр} = \frac{P_{внутр}}{G} = \frac{W_c}{g} + \frac{p_c F_c}{G}. \qquad (III.24)$$

In case of the absence of shock wave in nozzle because of the influence of external counterpressure p_0 the specific thrust, taken from internal contour, is equal to specific thrust in a vacuum, i.e.,

$$P_{уд.\,внутр} = P_{уд.\,п}.$$

Concerning the increase of specific thrust the first term in equation (III.23) or specific thrust, taken from the internal contour of combustion chamber (III.24) play a large part. Let us consider means of increasing the specific thrust, taken from the internal contour of the nozzle.

Decisive factor concerning increase of specific thrust $P_{уд.\,внутр}$ is increase of exit velocity

$$W_c = \sqrt{2g\frac{k}{k-1}RT_к\left[1-\left(\frac{p_c}{p_к}\right)^{\frac{k-1}{k}}\right]},$$

which depends on type of working medium ($RT_к$ and k) and expansion ratio of gases in the nozzle $\frac{p_к}{p_c}$. The larger the product of $RT_к$ and expansion ratio of gases in the nozzle, the higher the exit velocity is.

In rocket technology there are used both means of increasing exit velocity. Consequently, for increase of exit velocity, i.e., for increase of specific thrust $P_{уд.\ внутр}$, all other conditions being equal (see additional requirements for propellant in Chapter XVIII) one should use propellant with high value of $RT_к$ and increase the expansion ratio in the nozzle. It is possible to increase the gas exit velocity from the nozzle for prescribed propellant only by increase of expansion ratio $\frac{p_к}{p_c}$. The latter method of increase of W_c and $P_{уд}$ is widely applied in practice.

It is possible to increase the expansion ratio by lowering the pressure on the nozzle section, leaving pressure in the combustion chamber constant, or by increase of pressure in the chamber, leaving pressure on the nozzle section constant, or, finally, using both means taking into account the assignment of the liquid-propellant rocket engine.

On Fig. III.9 there are presented theoretical values of specific thrust in calculated conditions depending on gas expansion in the nozzle $\frac{p_к}{p_c}$ for several propellants.

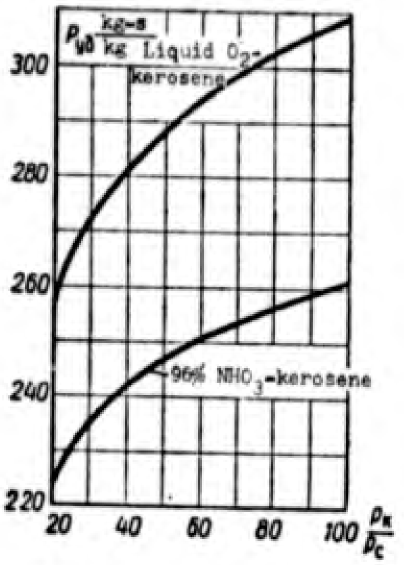

Fig. III.9. Dependence $P_{уд} = f\left(\frac{p_к}{p_c}\right.$ and type of propellant).

The assignment of the rocket determines what propellant to use. For contemporary liquid-propellant rocket engines depending on the propellant used the real specific thrust composes $P_{уд} \simeq 250-450$

(the last figure pertains to ZhRD which uses hydrogen as fuel).

Above there were examined means of increasing specific thrust, taken from the internal contour. This is widely used for liquid-propellant rocket engines of the second and third stages of rockets, and also for liquid-propellant rocket engines, operating in a medium where $p_0 > 0$, but with some specific character.

From formula (III.23) it is clear that with p_0 nonzero, specific thrust is determined not only by specific thrust taken from the internal contour, but also negative term $\frac{p_0 F_c}{G}$. In case of liquid-propellant rocket engine operation with $p_0 >> 0$ (liquid-propellant rocket engines of single-stage rockets, liquid-propellant rocket engines of the first stage of multistage rockets, etc.) it is impossible to arbitrarily decrease the pressure on the nozzle section for increase of expansion ratio for the purpose of increasing the exit velocity. With decrease of pressure on the nozzle section lower than ambient pressure, increase of specific thrust, taken from internal contour of the nozzle, does not compensate the negative influence of static term $\frac{p_0 F_c}{G}$. Here, just as for thrust, rated conditions $p_0 = p_c$ are optimum, but with all the observations which were made with respect to thrust at rated conditions.

§ 5. Basic Components of Thrust Forces of Combustion Chamber, Place of Their Application, Thrust Coefficient

Earlier there were determined calculated dependences for determination of thrust created by the entire combustion chamber. For analysis of operation of separate units of the combustion chamber, calculations for strength, determination of the most advantageous place for fastening the chamber to the propulsion system, and for evaluation of means of improvement of combustion chamber characteristic it is necessary for the designer to know what portion of thrust is taken from some part of the chamber and what are further possibilities for augmentation of thrust obtained from one kilogram of propellant, i.e., specific thrust. For analysis of thrust components and place of their application it is more convenient to represent thrust as is shown on Fig. III.10.

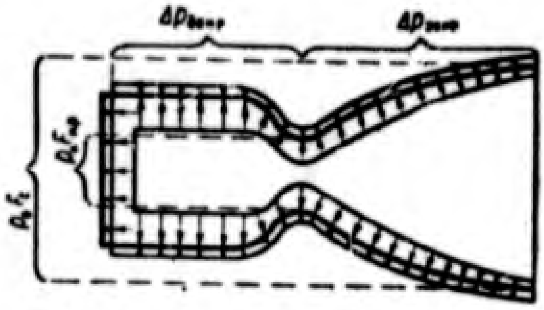

Fig. III.10. Place of application and thrust components.

As earlier, combustion chamber thrust is determined by equation (III.12).

The first integral of the equation can be presented in the form

$$P_{\text{внутр}} = p_{\text{к}} F_{\text{кр}} + \Delta P_{\text{докр}} + \Delta P_{\text{закр}}, \qquad \text{(III.25)}$$

where $p_{\text{к}} F_{\text{кр}}$ — unbalanced force, applied to combustion chamber head; $\Delta P_{\text{докр}}$ — force appearing because of large average pressure, affecting the annular element of the head $(F_{\text{к}} - F_{\text{кр}})$, as compared to average pressure affecting the subcritical part of the nozzle of the same area; $\Delta P_{\text{закр}}$ — force affecting the supercritical part of the nozzle.

The second integral of equation (III.12) determines the force appearing from ambient pressure on the external contour of combustion chamber, equal to $p_0 F_c$. Then thrust force can be represented from four components:

$$P = p_{\text{к}} F_{\text{кр}} + \Delta P_{\text{докр}} + \Delta P_{\text{закр}} - p_0 F_c.$$

For quantitative analysis of components of thrust forces, taken from the internal contour, it is expedient to convert equation (III.15) in the following way:

$$P_{\text{внутр}} = \frac{G}{g} W_c + p_c F_c = p_c F_c \left(1 + \frac{W_c G}{g p_c F_c}\right).$$

Further, using equalities

$$G = \gamma_c W_c F_c; \quad \frac{p_c}{\gamma_c} = RT_c; \quad M_c^2 = \frac{W_c^2}{kgRT_c},$$

where k – isentropic index,

we will obtain

$$P_{внутр} = p_c F_c (1 + kM_c^2). \tag{III.26}$$

Let us divide and multiply the right side of expression (III.26) by $p_к F_{кр}$, then

$$P_{внутр} = \frac{p_c}{p_к} \cdot \frac{F_c}{F_{кр}} p_к F_{кр} (1 + kM_c^2). \tag{III.27}$$

Let us introduce the concept of internal thrust coefficient of the combustion chamber

$$K_{внутр} = \frac{P_{внутр}}{p_к F_{кр}}. \tag{III.28}$$

The internal thrust coefficient characterizes how many times thrust taken from the internal surface of the combustion chamber is greater than thrust applied to the combustion chamber head on an area equal to the critical throat diameter. The thrust coefficient shows the role and portion of the nozzle in creating combustion chamber thrust.

Let us divide the left and right sides of equation (III.27) by $p_к F_{кр}$, then

$$K_{вн} = \frac{p_c}{p_к} \frac{F_c}{F_{кр}} (1 + kM_c^2) = f_c \frac{1}{\varepsilon} (1 + kM_c^2), \tag{III.29}$$

where f_c – dimensionless area of nozzle; ε – expansion ratio of gases in the nozzle.

Formula (III.29) can be converted to a convenient form for analysis and calculations, if all the values entering it are expressed through M_c number, through velocity coefficient λ_c, or through ratio $\frac{p_c}{p_к}$. After simple conversions there are obtained the following dependences of thrust coefficient $K_{внутр}$ on M_c, λ_c and $\frac{p_c}{p_к}$:

$$K_{внутр}=\left(\frac{2}{k+1}\right)^{\frac{k-1}{2(k+1)}}\frac{1+kM_c^2}{M_c\sqrt{1+\frac{k-1}{2}M_c^2}}; \qquad \text{(III.30)}$$

$$K_{внутр}=\left(\frac{2}{k+1}\right)^{\frac{1}{k-1}}\frac{\lambda_c^2+1}{\lambda_c}; \qquad \text{(III.31)}$$

$$K_{внутр}=2\left(\frac{2}{k+1}\right)^{\frac{1}{k-1}}\frac{k}{\sqrt{k^2-1}}\sqrt{1-\left(\frac{p_c}{p_к}\right)^{\frac{k-1}{k}}}\times$$

$$\times\left[1+\frac{k-1}{2k}\frac{\left(\frac{p_c}{p_к}\right)^{\frac{k-1}{k}}}{1-\left(\frac{p_c}{p_к}\right)^{\frac{k-1}{k}}}\right]. \qquad \text{(III.32)}$$

Now it is possible to proceed to quantitative analysis of thrust components. From formulas (III.30, III.32) it is clear that thrust coefficient $K_{внутр}$ depends only on the expansion ratio and index of the expansion process. From equation (III.25) there can be found $K_{внутр}$, having divided all its terms by $p_кF_{кр}$:

$$K_{внутр}=K_{внутр_1}+K_{внутр_2}+K_{внутр_3}.$$

where

$$\left.\begin{aligned}K_{внутр_1}&=\frac{p_к F_{кр}}{p_к F_{кр}}=1;\\ K_{внутр_2}&=\frac{\Delta P_{докр}}{p_к F_{кр}};\\ K_{внутр_3}&=\frac{\Delta P_{закр}}{p_к F_{кр}}.\end{aligned}\right\} \qquad \text{(III.33)}$$

which permits evaluating the role of separate elements of the chamber in creating thrust.

For determination of the portion of thrust taken from the subcritical part of the nozzle, let us consider the combustion chamber without the supercritical part of the nozzle. Having placed M = 1 in formula (III.30) or λ = 1 in formula (III.31), we will obtain the value of thrust coefficient of combustion chamber without the supercritical part of the nozzle

$$K_{\text{внутр}_{\lambda=1}} = 2\left(\frac{2}{k+1}\right)^{\frac{1}{k-1}}. \qquad \text{(III.34)}$$

In this case

$$K_{\text{внутр}_{\lambda=1}} = K_{\text{внутр}_1} + K_{\text{внутр}_2}.$$

From the formula it is clear that thrust coefficient $K_{\text{внутр}_{\lambda=1}}$ depends only on the index of expansion process, since with the presence of only the critical section the ratio of pressure in the chamber to pressure in the critical section is a constant value and is equal to

$$\beta_{\text{кр}} = \frac{p_{\text{кр}}}{p_{\text{к}}} = \left(\frac{2}{k+1}\right)^{\frac{k}{k-1}}.$$

Coefficient $K_{\text{внутр}_{\lambda=1}}$ at various k has the following values:

k	1,1	1,15	1,2	1,25	1,3
$K_{\text{внутр}_{\lambda=1}}$	1,206	1,224	1,230	1,250	1,260

Consequently, thrust force $\Delta P_{\text{докр}}$ composes 20-26% of thrust $p_{\text{к}}F_{\text{кр}}$ or $K_{\text{внутр}_2}$ equals 0.2-0.26. Thrust coefficient $K_{\text{внутр}_3}$ of supercritical part of the nozzle

$$K_{\text{внутр}_3} = K_{\text{внутр}} - K_{\text{внутр}_{\lambda=1}}. \qquad \text{(III.35)}$$

The portion of thrust taken from the supercritical part of the nozzle depends, as may be seen from formulas (III.30, III.32), on the expansion ratio of gases in the nozzle and is increased with growth of the latter. The portion of thrust taken from the supercritical part of the nozzle is 0.25-0.55 with change of $\frac{p_к}{p_c}$ from 10 to 100 and k = 1.15.

From the cited data it is clear that the portion of nozzle thrust reaches 80% of the so-called main thrust component $p_кF_{кр}$, i.e., the role of the nozzle in the creation of thrust, and consequently, specific thrust is especially great. It is necessary to emphasize that the value and role of the nozzle will continuously increase especially for liquid-propellant rocket engines of the second, third and higher stages of multistage rockets.

The situation consists of the following. Development of rocket technology is connected with the continuous growth of specific thrust of the rocket engine. One of the effective means for increasing specific thrust is increase of the expansion ratio of gases in the nozzle. Already there are liquid-propellant rocket engines, for which the expansion ratio reaches $\frac{p_к}{p_c}=500$ and more. Therefore, the portion of thrust taken from the nozzle continuously grows and can exceed the value of basic thrust component $p_кF_{кр}$. Naturally, even more emphasis will be placed on the improvement of the nozzle part of the chamber. Therefore, it is necessary to know what portion of thrust the combustion chamber nozzle on the whole and the supercritical part separately can give in the limit. For this, having assumed $\frac{p_к}{p_c}\to\infty$, in formula (III.32) we will obtain the maximum value of thrust coefficient

$$K_{внутр.\,max}=2\left(\frac{2}{k+1}\right)^{\frac{1}{k-1}}\frac{k}{\sqrt{k^2-1}}. \qquad \text{(III.36)}$$

Maximum portion of thrust taken from the supercritical part of the nozzle

$$K_{внутр\,max_c}=K_{внутр\,max}-K_{внутр\,\lambda=1}. \qquad \text{(III.37)}$$

Results of calculations are given in the table.

k	1.1	1.15	1.2	1.25	1.3
$K_{\text{внутр. max}}$	2.88	2.45	2.23	2.08	1.98
$(K_{\text{внутр}_2} + K_{\text{внутр}_3})_{\max}$	1.88	1.45	1.23	1.08	0.98
$K_{\text{внутр. max}_3}$	1.67	1.23	1.00	0.83	0.72

From the given table it is clear that the portion of thrust obtained from the combustion chamber nozzle $K_{\text{внутр}_2} + K_{\text{внутр}_3}$ in the limit (when $\frac{p_k}{p_c} \to \infty$), when k = 1.15 (the closest index of expansion process for contemporary propellants), exceeds the basic thrust component $p_k F_{\text{кр}}$ one and a half times. Naturally, no one will make a nozzle with $\frac{p_k}{p_c} \to \infty$, but it should be emphasized that the intensive growth of the portion of thrust taken from the supercritical part of the nozzle lies in technically feasible limits of expansion ratio $\frac{p_k}{p_c}$ (on the order of several thousands of units). Therefore, the portion of thrust taken from the nozzle will exceed the basic component of thrust force $p_k F_{\text{кр}}$, receiving the name basic in the initial period of development of rocket technology, when values of expansion ratio were small (on the order of $\frac{p_k}{p_c} = 20-30$) and the portion of the nozzle in the creation of combustion chamber thrust was significant. On Fig. III.11 there is presented the dependence of change of the portion of thrust taken from the internal surface of the combustion chamber, depending on expansion ratio $\frac{p_k}{p_c}$ at constant pressure in the combustion chamber.

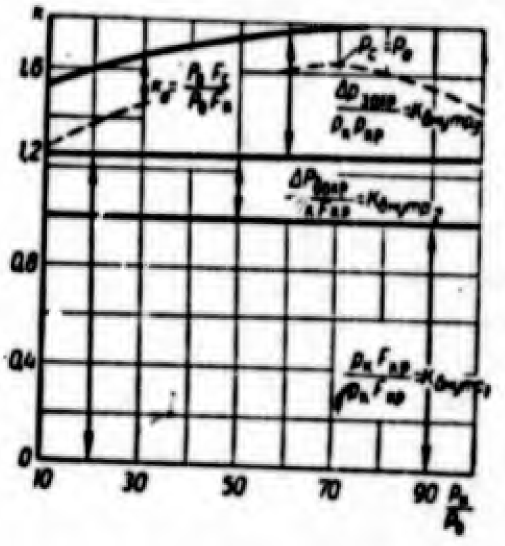

Fig. III.11. Dependence of thrust component on $\frac{p_k}{p_c}$.

Having considered portions of thrust taken from separate parts of the combustion chamber in the absence of ambient pressure, let us examine the influence of external counterpressure on the thrust coefficient. Having divided the left and right sides of equation (III.11) by $p_кF_{кр}$, we will obtain the value of nozzle thrust coefficient K taking into account counterpressure

$$K = K_{внутр} - K_0 \qquad \text{(III.38)}$$

where $K_0 = \frac{p_0F_c}{p_кF_{кр}}$ — the portion of thrust taken from the external surface of combustion chamber with respect to $p_кF_{кр}$, or

$$K = K_{внутр} - \frac{p_0}{p_к} f_c. \qquad \text{(III.39)}$$

From the formula it is clear that it is impossible to arbitrarily increase $K_{внутр}$ by increasing the expansion ratio $(\frac{p_к}{p_c})$ at prescribed pressure in the chamber due to lowering of pressure on the nozzle section for liquid-propellant rocket engines, for which part or all the trajectory passes in the atmosphere.

From determination of thrust coefficient it follows that the character of change of the value of thrust coefficient K from pressure on the nozzle section is analogous to character of change of thrust force from pressure on the nozzle section. Figure III.11 shows the character of change of thrust coefficient K depending on expansion ratio (dimensionless area of nozzle) when $p_к = \text{const}$.

Just as thrust, thrust coefficient K is decreased with deviation of nozzle operating conditions from rated conditions, and the intensity of change of K is decreased with increase of pressure in the combustion chamber.

§ 6. Thrust and Specific Thrust of Liquid-Propellant Rocket Engine

In the preceding sections there were examined calculated dependences and regularities of change of combustion chamber thrust and specific thrust. All formulas for calculation of thrust and specific thrust, and also the character of their change from some parameters will be valid for liquid-propellant rocket engines if propellant combustion products enter the atmosphere only through the combustion chamber. Such liquid-propellant rocket engines include engines with pressurized fuel feed system and engines with turbopump unit, working medium of which is burned in the combustion chamber.

In a number of liquid-propellant rocket engines with turbopump unit the basic or auxiliary propellants are used for generation of working medium of turbine with its subsequent discharge into the environment.

If the working medium of the turbopump unit turbine is discharged into the environment without the use of exhaust reaction, then liquid-propellant rocket engine thrust is practically equal to combustion chamber thrust, and specific thrust

$$P_{уд.д} = \frac{P_{к.с}}{G+G_{т.т}} = \frac{P_{уд.к.с}}{1+\xi}, \qquad \text{(III.40)}$$

where $G_{т.т}$ — propellant flow rate to turbine;
$P_{уд.к.с}=\frac{P_{к.с}}{G}$ — specific thrust of combustion chamber;
$\xi=\frac{G_{т.т}}{G}$ — relative portion of propellant flow rate to turbine.

From formula (III.40) it is clear that in this case the specific thrust of the propulsion system is always less than specific thrust of combustion chamber. Value of ξ is determined on the basis of calculation of the turbopump unit turbine or on the basis of statistical data. The value of ξ for liquid-propellant rocket engines with exit of working medium from the turbopump unit into the environment reaches 4-5%, which is a very large value. With exit of working medium from the turbopump unit into the environment for the purpose of decreasing specific thrust losses of liquid-propellant rocket engines the working medium of the turbine is directed into special ejector exhaust pipes (in a number of liquid-propellant rocket engines these ejector pipes serve for control and correction of rocket flight), which create small additional thrust. In this case thrust force of liquid-propellant rocket engine is calculated by equation

$$P = P_{\text{к.с}} + P_{\text{р.в.п}}, \tag{III.41}$$

where $P_{\text{р.в.п}}$ — thrust created by ejector exhaust pipes.

Calculation of both combustion chamber thrust and thrust force, created by ejector exhaust pipes, is performed by usual formulas, for example by formula (III.11).

Specific thrust of propulsion system is determined by formula

$$P_{\text{уд.д}} = \frac{P_{\text{к.с}} + P_{\text{р.в.п}}}{G + G_{\text{т.т}}} = P_{\text{уд.к.с}} \frac{1 + \frac{P_{\text{р.в.п}}}{P_{\text{к.с}}}}{1 + \xi}. \tag{III.42}$$

It is necessary to emphasize that ejection of the working medium through ejector pipes only partially improves the ZhRD characteristics — thrust and specific thrust, since propellant in the gas generator for the turbine burns at nonoptimal α for the purpose of obtaining permissible gas temperatures on turbine blades. Therefore

$$P_{\text{уд.д}} < P_{\text{уд.к.с}}.$$

For decrease of these specific thrust losses we went to designs of liquid-propellant rocket engines where the working medium of the turbine is burned in the combustion chamber.

§ 7. Methods of Evaluating the Degree of Perfection of the Working Process in the Combustion Chamber

As in every thermal unit, definite losses exist in the combustion chamber, leading to decrease of its specific thrust. Decrease of specific thrust is connected with specific types of thermal, chemical, and gas-dynamic losses in the combustion chamber. Some losses can be eliminated, for example incomplete combustion of propellant in the predetermined volume of combustion chamber because of poor organization of carburetion, others, for example gas friction losses on nozzle walls of combustion chamber, cannot be eliminated, and can only be decreased due to decrease of friction surface (for example, by application of profiled nozzles).

It is accepted to evaluate all types of losses in the combustion chamber, which lead to decrease of its specific thrust, with the aid of specific thrust coefficient of the combustion chamber

$$\varphi_{\text{уд}} = \frac{(P_{\text{уд. внутр}})_{\text{э}}}{(P_{\text{уд. внутр}})_{\text{т}}}, \tag{III.43}$$

where $(P_{\text{уд. внутр}})_{\text{э}}$ and $(P_{\text{уд. внутр}})_{\text{т}}$ — experimental and theoretical values of specific thrust when $p_0 = 0$. Theoretical value of $(P_{\text{уд. внутр}})_{\text{т}}$ is calculated by formula (III.24). Experimental value of $(P_{\text{уд. внутр}})_{\text{э}}$ is determined on the basis of experimental data. By knowing from experiment $P_{\text{э}}$, propellant flow rate, ambient pressure and area of nozzle exit section F_c, one can determine $P_{\text{уд. внутр}}$ by means of conversion by formula

$$(P_{\text{уд. внутр.}})_{\text{э}} = \frac{P_{\text{внутр. э}}}{G_{\text{э}}} = \frac{P_{\text{э}} + p_0 F_c}{G_{\text{э}}}. \tag{III.44}$$

For contemporary combustion chambers the specific thrust coefficient $\varphi_{\text{уд}} = 0{,}95 - 0{,}97$. A similar method permits evaluating the degree of perfection of the created combustion chamber on the whole. In case of small value of $\varphi_{\text{уд}}$ the designer should know for what reasons there appeared considerable specific thrust losses, and should eliminate the defect. Below there is cited a method of evaluating specific thrust losses of combustion chamber.

§ 8. Evaluation of Degree of Perfection of Working Process Strictly in the Combustion Chamber

Evaluation of degree of perfection of the working process in the chamber without its nozzle unit is performed with the aid of the ratio of actual to theoretical chamber pressure. For this let us introduce the idea of specific impulse of pressure in the combustion chamber.

From thermodynamic and gas-dynamic calculation the flow rate of combustion chamber products through the chamber can be determined by formula

$$G=\sqrt{kg}\left(\frac{2}{k+1}\right)^{\frac{k+1}{2(k-1)}}\frac{p_{\text{к}}F_{\text{кр}}}{\sqrt{RT_{\text{к}}}}=A\frac{p_{\text{к}}F_{\text{кр}}}{\sqrt{RT_{\text{к}}}},$$

where $A=\sqrt{kg}\left(\frac{2}{k+1}\right)^{\frac{k+1}{2(k-1)}}$ — value depending only on index of expansion process constant for a concrete engine.

Having divided the left and right sides of the first equation by $p_{\text{к}}F_{\text{кр}}$, we will obtain

$$\beta=\frac{\sqrt{RT_{\text{к}}}}{A}, \qquad \text{(III.45)}$$

where $\beta=\frac{p_{\text{к}}F_{\text{кр}}}{G}$ — specific impulse of pressure in the combustion chamber.

Product of $p_{\text{к}}F_{\text{кр}}$ represents the main component of thrust force. Relationship of $p_{\text{к}}F_{\text{кр}}$ to propellant flow rate per second has dimensionality of specific thrust and represents specific thrust component of the combustion chamber. Specific impulse of combustion chamber pressure is made up of combustion chamber parameters, not depending on nozzle parameters. Specific impulse of pressure depends on the excess oxidant ratio α and insignificantly on the pressure in combustion chamber due to its influence on the value of degree of dissociation of combustion products.

From the thermodynamic calculation of combustion chamber there is known the theoretical value of $\beta_{\text{т}}$, and from experiment (by measuring $p_{\text{к}}$, $F_{\text{кр}}$ and G) — value of $\beta_{\text{э}}$. Relationship of experimental value of $\beta_{\text{э}}$ to its theoretical value carries the name <u>ratio of actual to theoretical chamber pressure</u> and characterizes the degree of perfection of working process in the combustion chamber

$$\varphi_{\beta}=\frac{\beta_{\text{э}}}{\beta_{\text{т}}}. \qquad \text{(III.46)}$$

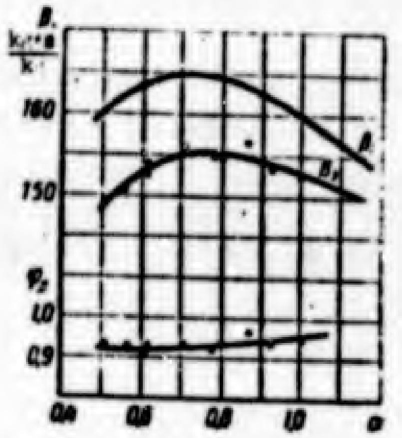

Fig. III.12. Experimental dependence β, $\varphi_\beta = f(\alpha)$.

In contemporary chambers

$$\varphi_\beta = 0.95 : 0.99.$$

Figure III.12 shows results of experimental determination of the ratio of actual to theoretical chamber pressure. Coe[illegible]cients ϕ_β estimate the incompleteness of heat liberation in the combustion chamber. In case of low values of ϕ_β it is necessary to improve the process of carburetion or, if this turned out to be insufficient for increase of ϕ_β, to increase the volume of combustion chamber. It is necessary to note that the method of increase of ϕ_β by increase of the chamber volume is undesirable, since it leads to increase of weight, chamber dimensions and others. This method can be used only when all the possibilities of increasing ϕ_β by improvement of the carburetion system are exhausted.

§ 9. Evaluation of the Degree of Perfection of the Working Process in the Combustion Chamber Nozzle

For evaluation of the degree of perfection of the working process in the nozzle let us use the idea of thrust coefficient $K_{п,тр}$. Earlier it was shown that thrust coefficient $K_{п,тр}$ characterizes the portion of thrust created by the nozzle $p_0 = 0$, the value of which does not depend on the course of the working process in combustion chamber and is completely determined by nozzle parameters. Theoretical value of thrust coefficient $K_{п.тр.т}$ can be determined on the basis of thermodynamic and gas-dynamic calculation of the combustion chamber by formula (III.32), and its experimental value — according to test data of the combustion chamber. Ratio of experimental value of thrust coefficient to its theoretical value determines the degree of perfection of the working process in the combustion chamber nozzle:

$$\varphi_c = \frac{(K_{\text{внутр}})_\text{э}}{(K_{\text{внутр}})_\text{т}}. \qquad \text{(III.47)}$$

According to determination the experimental value of $(K_{\text{внутр}})_\text{э}$ is equal to

$$K_{\text{внутр. э}} = \frac{P_{\text{внутр. э}}}{p_\text{к} F_{\text{кр}}} = \frac{P_\text{э} + p_0 F_c}{p_\text{к} F_{\text{кр}}}. \qquad \text{(III.48)}$$

By knowing from experiment the value of thrust $P_\text{э}$, pressure in combustion chamber $p_\text{к}$ and environment, and geometric dimensions of combustion chamber nozzle F_c and $F_{\text{кр}}$, let us determine the experimental value of $(K_{\text{внутр}})_\text{э}$; having theoretical and experimental values of thrust coefficient $K_{\text{внутр}}$, let us determine the value of losses ϕ_c in combustion chamber nozzle. In contemporary combustion chambers ϕ_c = 0.96-0.98. Large values of ϕ_c pertain to profiled nozzles. It is necessary to emphasize that coefficient ϕ_c estimates all losses in the nozzle (friction losses, nonparallel outflow, nonisentropy of expansion process and various types of gas-dynamic losses).

Using dependences (III.28, III.39, III.46, III.47), formulas for calculation of thrust and specific thrust will take the form

$$P = \varphi_c K_{\text{внутр. теор}}\, p_\text{к} F_{\text{кр}} - p_0 F_c,$$

$$P_{\text{уд}} = \varphi_\text{э} \beta_{\text{теор}} \left(\varphi_c K_{\text{внутр. теор}} - \frac{p_0}{p_\text{к}} f_c\right).$$

§ 10. Calculation of Thrust with the Presence of Shock Wave in the Combustion Chamber Nozzle

The earlier obtained dependence for calculation of basic combustion chamber parameters (thrust, specific thrust and others) are valid under the condition of independence of working process in the chamber, including its nozzle, from ambient pressure.

The working process in the chamber nozzle does not depend on ambient pressure underexpansion conditions, rated conditions and up to specific times in overexpansion conditions. Flow parameters of gas stream are changed only for the nozzle, in free supersonic stream.

With definite overexpansion of gas in the nozzle on its section there will be formed a bridge-like shock wave, which consists (Fig. III.13) of two oblique shock waves a-b and b-c and central jump of variable intensity b-d. G. I. Petrov showed that the bridge-like shock wave can travel into the depth of the nozzle, while not being converted into normal shock, assuming that at point b of intersection of three shock waves there is started a line of tangential discontinuity of velocities, and static pressures on both sides of the line of discontinuity are identical. In a number of works it was shown that the shock wave starts to move into the depth of the nozzle at some ratio of static pressures on the shock wave, depending on state of boundary layer and Mach number before the shock wave.

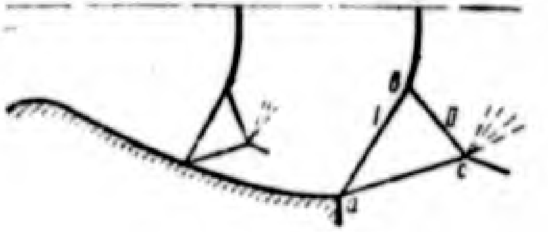

Fig. III.13. Diagram of operation of nozzle with shock wave.

Figure III.14 shows the dependence of critical static pressure ratio p_1/p_2 (p_1 and p_2 are pressure before and after shock wave respectively) on M_{cx} number of incoming flow before shock wave, obtained for turbulent boundary layer with number $Re_s = 5\cdot10^5-7\cdot10^7$.

For calculation of thrust and specific thrust of the chamber it is necessary to know the position of shock wave and regularities of change of gas flow parameters after the shock wave. In view of complexity of the process at present there is no reliable method of calculation for determining the position of shock wave and regularities of change of gas flow parameters after the shock wave. In view of complexity of the process at present there is no reliable method of calculation for determining the position of shock wave and regularities of change of gas flow parameters after the shock wave.

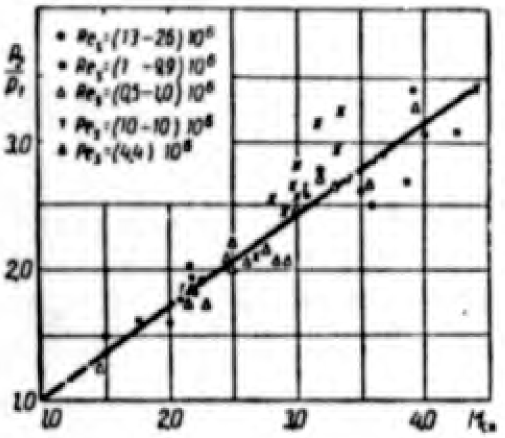

Fig. III.14. Dependence of critical ratio $p_2/p_1 = f(M)$.

At present it is expedient to perform calculation on the basis of semiempirical dependences, making it possible to determine more exactly the location of shock wave and gas flow parameters after shock, on the accuracy of determination of which depends the accuracy of determination of thrust and specific thrust of the combustion chamber. It was established that if pressure after the shock wave p_2 equals ambient pressure, then the position of shock wave is determined by relationship $\frac{p_2}{p_1}=f(M_{\text{cx}})$. Similar conditions are realized for nozzles with large apex angles $2\alpha \geq 30$ (see Fig. III.14). With decrease of nozzle cone angle and penetration depth of shock in the nozzle, the pressure after the shock wave can differ from the ambient pressure by several times. Figure III.15 shows how pressure recovery is changed after the shock wave depending on nozzle cone angle and depth of its penetration in the nozzle. In this case the position of shock is determined not only by critical static pressure ratio, but also by degree of pressure recovery after the shock wave. With the help of dependence $\frac{p_2}{p_1}=f(M_{\text{cx}})$ (see Fig. III.14), by knowing relationship $\frac{p_2}{p_0}=f(M_{\text{cx}};\ 2\alpha)$ (Fig. III.15), it is possible to construct dependence of the position of shock wave for nozzles with various geometric characteristics by relationship

$$\frac{p_0}{p_{\text{н}}}=\frac{p_0}{p_2}\cdot\frac{p_2}{p_1}\cdot\frac{p_1}{p_{\text{н}}}. \qquad \text{(III.49)}$$

Ratio $\frac{p_1}{p_{\text{н}}}$ is determined from condition of isentropic gas expansion in the nozzle, p_2/p_1 – by the graph of Fig. III.14, and p_0/p_2 – by the graph of Fig. III.15.

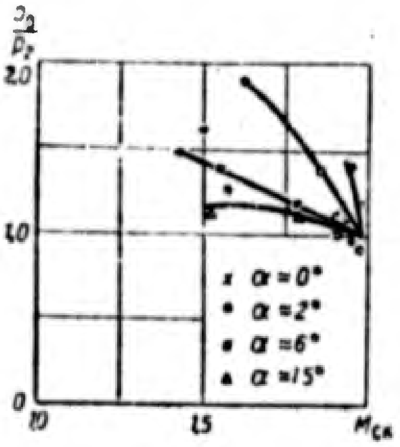

Fig. III.15. Pressure recovery after shock when $2\alpha < 30°$.

In case of the absence of pressure recovery after shock wave $p_2 = p_0$ equation (III.49) will take the form

$$\frac{p_0}{p_к} = \frac{p_1}{p_к} : \frac{p_1}{p_2}. \qquad \text{(III.50)}$$

By equation (III.50) there is constructed dependence of position of shock wave: $M_{с.к} = f\left(\frac{p_к}{p_0}\right.$ and k) (Fig. III.16). If dependence $\frac{p_0}{p_2} = f(M_{ск}$ and 2α) is unknown, and dependence $M_{ск} = f\left(\frac{p_к}{p_0}\right)$ is known, then we can find the value of p_0/p_2 by equation

$$\frac{p_0}{p_2} = \frac{p_0}{p_к} \cdot \frac{p_1}{p_2} \frac{p_к}{p_1}. \qquad \text{(III.51)}$$

By knowing the value of $M_{ск}$ and p_2, we can determine thrust and specific thrust of the combustion chamber. Thrust taken from the internal contour can be represented as thrust taken before and after the shock wave:

$$P_{внутр} = \int\limits_{s_{внутр}} p\,ds\cos\left(\overset{\wedge}{n\,x}\right) = \int\limits_{s_{внутр.д.с}} p_i\,ds\cos\left(\overset{\wedge}{n\,x}\right) + \int\limits_{F_{ск}}^{F_c} p_i\,dF, \qquad \text{(III.52)}$$

where $s_{внутр.д.с}$ — chamber surface before shock wave; $F_{ск}$ — area of nozzle where shock is located.

Determination of $\int\limits_{s_{внутр.д.с}} p_i\,dS\cos(\overset{\wedge}{nx})$ is produced by usual dependences, since before the shock wave there occurs usual gas flow in the nozzle and then

$$\int\limits_{s_{внутр.д.с}} p_i\,ds\cos\left(\overset{\wedge}{n\,x}\right) = p_{1ск}F_{ск}(1 + kM_{ск}^2). \qquad \text{(III.53a)}$$

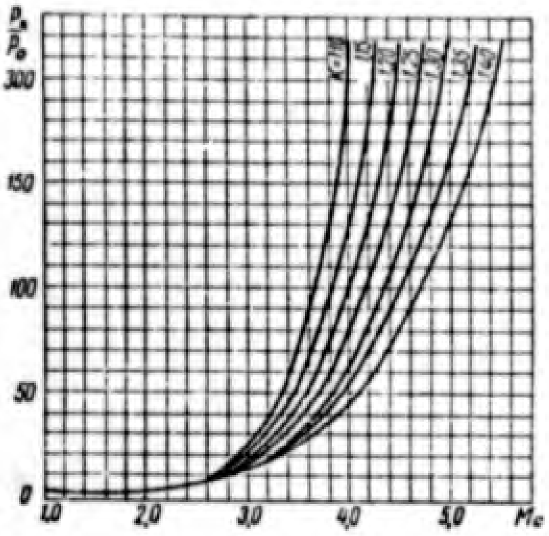

Fig. III.16. Dependence of position of shock wave on $\frac{p_к}{p_0}$ and k.

where $p_{1сж}$ — calculated pressure before shock wave; $M_{сж}$ — M number before shock wave.

When $p_2 = p_0$ the value of integral $\int_{F_{сж}}^{F_c} p_i dF$ is equal to

$$\int_{F_{сж}}^{F_c} p_0\, dF = p_0 (F_c - F_{сж}). \qquad \text{(III.53b)}$$

When $p_2 \neq p_0$ the determination of $\int_{F_{сж}}^{F_c} p_i dF$ is complicated by ignorance of the character of pressure recovery after the shock wave, but proceeding from experimental data it is known that the pressure on the nozzle section equals ambient pressure. Therefore, one can determine the average pressure affecting the nozzle walls from the position of shock wave to the nozzle section:

$$p_{ср} = \frac{p_1 + p_0}{2},$$

then

$$\int_{F_{сж}}^{F_c} p_i\, dF = p_{ср} (F_c - F_{сж}). \qquad \text{(III.53c)}$$

Thrust obtained from the external contour of the chamber is equal to

$$P_{внеш} = p_0 F_c. \qquad \text{(III.54)}$$

By using dependences (III.52, III.53a, b, c) expressions can be obtained for computing thrust and specific thrust of the combustion chamber at nozzle operating conditions with shock wave:

a) for nozzles with large ($2\alpha \geq 30°$) apex angles or for small penetration of shock into the nozzle depth, i.e., for $p_2 = p_0$:

$$P = p_{1\text{сж}} F_{\text{сж}} (1 + kM^2_{\text{сж}}) - p_0 F_{\text{сж}}; \qquad \text{(III.55)}$$

$$P_{\text{уд}} = \frac{p_{1\text{сж}} F_{\text{сж}} \left(1 + kM^2_{\text{сж}}\right)}{G} - \frac{p_0 F_{\text{сж}}}{G}; \qquad \text{(III.56)}$$

b) for nozzles with small apex angles and large penetration of shock into nozzle depth, i.e., $p_2 \neq p_0$:

$$P = p_{1\text{сж}} F_{\text{сж}} \left(1 + kM^2_{\text{сж}}\right) + p_{\text{ср}} (F_{\text{с}} - F_{\text{сж}}) - p_0 F_{\text{с}}; \qquad \text{(III.57)}$$

$$P_{\text{уд}} = \frac{p_{1\text{сж}} F_{\text{сж}} \left(1 + kM^2_{\text{сж}}\right)}{G} + \frac{p_{\text{ср}} (F_{\text{с}} - F_{\text{сж}})}{G} - \frac{p_0 F_{\text{с}}}{G}. \qquad \text{(III.58)}$$

It is necessary to note that by experimental data, obtained at nozzle operating conditions with shock wave, it is impossible to determine the value of specific thrust and thrust force in a vacuum by formula (III.44).

In this case results of calculation of thrust and specific thrust will give value of thrust $P_{\text{внутр}}$ and specific thrust $P_{\text{уд. внутр}}$, taken from internal contour at concrete counterpressure, and they have no relation to thrust and specific thrust in a vacuum.

CHAPTER IV

ZhRD CHARACTERISTICS

General Information

Dependences of thrust and specific thrust on any parameters, changed in the process of ZhRD operation, are called characteristics of liquid-propellant rocket engine.

Thrust and specific thrust of liquid-propellant rocket engines are affected by the relationship of components, flight speed of rocket, flight altitude of rocket and change of propellant flow rate in the combustion chamber.

Let us first make a number of observations about the effect of the first two factors on thrust and specific thrust. Propellant mixture ratio α during liquid-propellant rocket engine operation is kept constant for the purpose of obtaining optimum rocket parameters (for example, maximum range at prescribed nominal rocket weight). Therefore, it is inexpedient to investigate the effect of α on liquid-propellant rocket engine characteristics. In a case when the propellant mixture ratio is changed in the process of operation of ZhRD, it is easy to consider the effect of α on the course of ZhRD characteristics, by knowing the known dependences of specific thrust on the propellant mixture ratio. In most cases the rocket flight speed does not affect the ZhRD characteristics.

During rocket motion in a vacuum the thrust and specific thrust are fully determined according to equations (III.24) and (III.15) by working process parameters of the liquid-propellant rocket engine and do not depend on flight speed of the rocket.

During rocket motion in a medium with definite pressure two cases can be represented. At supersonic rocket speeds at its stern (Fig. IV.1) there is formed a region with pressure p_0' which is less than ambient pressure and is called base pressure. If at prescribed ambient pressure p_0 a shock wave does not enter the nozzle, i.e., the working process in the chamber is isolated from ambient pressure, then thrust and specific thrust do not depend on flight speed of the rocket and their values are calculated by equations (III.11), (III.23). In practice there can be encountered a case when at ambient pressure p_0 a shock wave enters the nozzle and thrust and specific thrust should be calculated by equations (III.55, III.57),(III.56, III.58). It is known that all other conditions being equal the position of shock wave and value of pressure behind it, values of which affect the value of thrust and specific thrust, depend on the pressure of medium where the gas flow from the nozzle goes.

Base pressure depends on the rocket speed, and consequently, in this case thrust and specific thrust also depend on the speed of rocket motion, since the position of shock wave and pressure behind the shock wave depend not on ratio $\frac{p_k}{p_0}$, but on $\frac{p_k}{p_0'}$. The case when thrust and specific thrust depend on rocket speed is realized very rarely and only on an insignificant part of the rocket trajectory, therefore this case will not be examined in detail. Change of propellant flow rate to the ZhRD chamber and ambient pressure have the greatest effect on thrust and specific thrust.

On the basis of that mentioned above, at present two liquid-propellant rocket engine characteristics are of practical interest.

1. Consumption (throttle) characteristic, which shows change of thrust and specific thrust of a liquid-propellant rocket engine depending on propellant consumption at constant propellant mixture

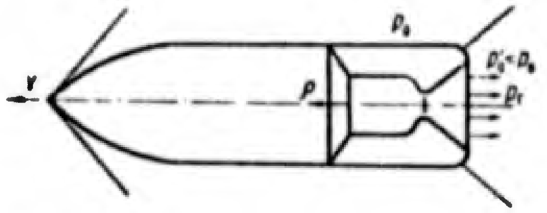

Fig. IV.1. For explanation of base pressure p_0'.

ratio and ambient pressure.

2. Altitude performance, which shows change of thrust and specific thrust depending on ambient pressure at constant consumption and mixture ratio.

In most cases in the process of rocket flight the liquid-propellant rocket engine operates at variable propellant consumptions and ambient pressures. Thus, for example, a liquid-propellant rocket engine operating on anergolic components, installed on a long-range rocket, has the following character of thrust change (Fig. IV.2).

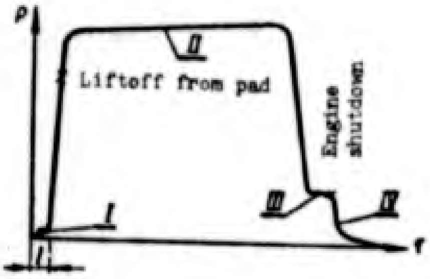

Fig. IV.2. Dependence of thrust engine change on time.

On preliminary stage I the liquid-propellant rocket engine has very low propellant consumption to ensure smooth approach of the liquid-propellant rocket engine to normal rating. Time of operation at preliminary stage is insignificant (about one second). Further, flow rate to the chamber increases to nominal – liquid-propellant rocket engine approaches main stage II, duration of which is the basic operating time of the liquid-propellant rocket engine. At the main stage consumption is kept constant, but ZhRD thrust increases due to decrease of ambient pressure along the path of rocket travel.

Before ZhRD cutoff there again occurs decrease of flow rate of propellant to the combustion chamber – ZhRD transfers from main stage conditions to conditions of final stage III, thrust of which is about 30% of thrust on the main stage. At this mode the rocket reaches rated parameters (for example, rated velocity), after which the command is given to cut off the liquid-propellant rocket engine. The automatic flight control system ceases its operation.

Section IV dependence $P = f(\tau)$ characterizes the change of thrust after the command is given to shut fuel valves due to inertness of operation of cutoff valves, propellant leakage, filling the hydraulic lines past the cutoff valves, and so forth.

It is necessary to distinguish the characteristics of combustion chamber and liquid-propellant rocket engine. In a case when all the propellant enters the combustion chamber (liquid-propellant rocket engine with pressurized fuel feed, liquid-propellant rocket engine with pump fuel feed system, working on a closed scheme and so forth), combustion chamber characteristics are simultaneously also ZhRD characteristics. For ZhRD with pump fuel feed at open scheme the combustion chamber characteristics differ from ZhRD characteristics inasmuch as part of the propellant is used for generation of turbine working medium with its subsequent ejection into the environment. The latter case will be examined separately at the end of the chapter.

§ 1. Consumption Characteristic

Consumption characteristics will be studied under the assumption of invariability of the working process in the combustion chamber ($\varphi_{\text{з}} = \text{const}$ and $\varphi_{c} = \text{const}$) and with ratio $\frac{p_0}{p_{\text{н}}}$, when the flow rate of gas through the chamber nozzle does not depend on ambient pressure and in the nozzle throat is always speed of sound. Engine operating conditions when the flow rate of combustion products through the chamber depends on ambient pressure, will not be examined, since similar conditions are practically not encountered in operation.

It is expedient to consider the engine consumption characteristic in a vacuum ($p_0 = 0$) and in the presence of ambient pressure p_0.

During operation in a vacuum thrust and specific thrust are determined by equations (III.13) and (III.24):

$$P_{п} = P_{внутр} = \frac{W_c}{g} G + p_c F_c;$$

$$P_{уд.п} = P_{уд.внутр} = \frac{W_c}{g} + \frac{p_c F_c}{G}.$$

Usually in practice there is constructed the dependence of thrust and specific thrust not on propellant consumption in the chamber, but on pressure in the chamber. The latter is explained by the fact that for a concrete engine the propellant consumption linearly depends on pressure in the combustion chamber (considering the earlier introduced assumption, $\varphi_\beta = \text{const}$).

Actually, by using the idea of specific impulse (III.45), we obtain

$$G = \frac{p_к F_{кр}}{\beta} = c p_к; \tag{IV.1}$$

since for concrete engine $F_{кр} = \text{const}$, $\beta = \text{const}$ and $\frac{F_{кр}}{\beta} = \text{const}$.

From equation (IV.1) it follows that propellant consumption is directly proportional to combustion chamber pressure. Fig. IV.3 shows the dependence of combustion chamber pressure on propellant

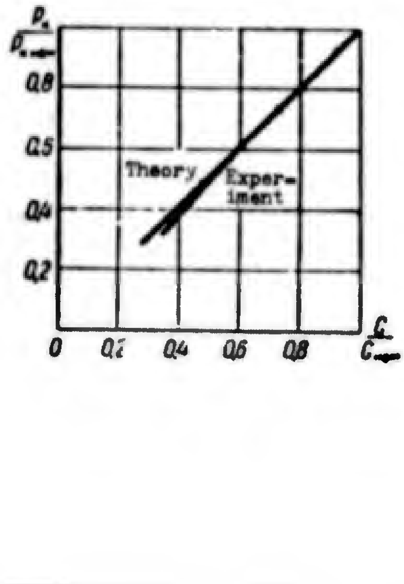

Fig. IV.3. Dependence $p_к = f(G)$.

consumption. For the figure it is clear that chamber pressure is changed directly proportional to the change of propellant consumption. Deviation of experimental dependence from theoretical $p_K = f(G)$ at low p_K is explained by impairment of working process (φ_β) in the combustion chamber in connection with deterioration of propellant atomization because of decrease of pressure drop on injectors and increase of degree of dissociation of combustion products. For well broken-in engines the difference of theoretical and experimental dependences $p_K = f(G)$ in the existing limits of thrust change with respect to consumption characteristic is small.

At the same time, pressure in the combustion chamber more visually characterizes change of engine conditions and for many units is the master parameter. Furthermore, chamber pressure is measured more exactly than the propellant consumption.

In practice the consumption characteristic is constructed according to pressure in the combustion chamber. For formulation of equation of consumption characteristic in a vacuum let us substitute the value of G from formula (IV.1) in formula (III.13), and, considering that dimensionless nozzle area f_c, expansion ratio $\varepsilon = \frac{p_к}{p_c}$ and V_c are constants for a concrete engine, without taking dissociation of combustion products into account we will obtain the formula for calculation of consumption characteristic

$$P_{\text{пустр}} = c_1 p_к, \tag{IV. 2}$$

where

$$c_1 = c\frac{w_c}{g} + \frac{F_c}{\varepsilon}.$$

From formula (IV.2) it is clear that thrust in a vacuum is directly proportional to pressure in the combustion chamber. It is expressed graphically by a straight line, passing through the origin of coordinates (Fig. IV.4). Having divided the left and right sides of equation (IV.2) by propellant consumption and using formula (VI.1), we obtain the dependence for calculation of specific thrust in a vacuum

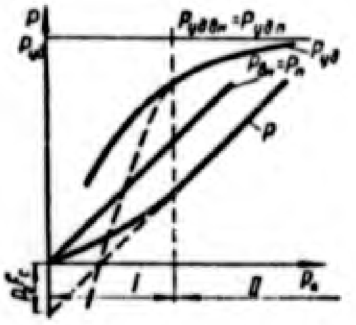

Fig. IV.4. Dependence of thrust $P_{\text{внутр}} = f(p_к)$ when $p_0=0$

during engine operation on consumption characteristic

$$P_{\text{уд. внутр}} = \frac{P_{\text{внутр}}}{G} = \frac{c_1 p_к}{c p_к} = c_2.$$

where

$$c_2 = \frac{c_1}{c} = \text{const}. \qquad \text{(IV. 3)}$$

From formula (IV.3) it is clear that specific thrust in a vacuum does not depend on pressure in the combustion chamber, of course at the assumptions on whose basis consumption characteristics were constructed. In reality, with decrease of pressure in the combustion chamber, especially at low pressures, the working process deteriorates, degree of dissociation of combustion products increases, and thrust and specific thrust will be less than rated. Further, let us examine peculiarities of the course of consumption characteristic at some ambient pressure.

Course of consumption characteristic essentially depends on the character of the effect of counterpressure on nozzle operating conditions. It is known that depending on intrachamber parameters, the working process in the nozzle can be independent of ambient pressure and can depend on it — in the latter case a shock wave enters the nozzle.

Up to the moment of entry of shock wave in the nozzle thrust and specific thrust are determined by equations:

$$P = P_{\text{внутр}} - p_0 F_c;$$

$$P_{\text{уд}} = \frac{P_{\text{внутр}}}{G} - p_0 \frac{F_c}{G}.$$

or, by using formulas (IV.2) and (IV.3), we obtain

$$P = c_1 p_{к} - F_c p_0; \qquad \text{(IV.4)}$$

$$P_{уд} = c_2 - \frac{F_c p_0}{G}. \qquad \text{(IV.5)}$$

From formula (IV.4) it follows that in this case thrust, as in a vacuum, linearly depends on pressure in the combustion chamber and is graphically (Fig. IV.4) represened by a straight line, but shifted downwards to value p_0F_c from P_{Γ} (zone II).

With decrease of pressure in the combustion chamber, the specific thrust will drop in connection with the growth of absolute value of negative term $\frac{p_0F_c}{G}$, which one can well see from Fig. IV.4. With the absence of shock wave in the nozzle it is possible to use formulas (III.16), (III.44) for calculation of thrust and specific thrust in a vacuum according to the results of engine tests with some counterpressure, for example with atmospheric, since thrust is taken from the internal contour, and is not changed with change of ambient pressure. Starting from some pressure $p_{к}$, a shock wave enters the nozzle and the use of formulas (IV.4) and (IV.5), valid in the absence of shock wave, is impossible, since the formal use of these formulas leads to incorrect derivations. Thus, for example, with an inoperative engine, i.e., when $p_{к} = 0$, the engine develops negative thrust, which is physically impossible. It is necessary to note that fictitious point $-p_0F_c$ is useful for construction of consumption characteristic in the region of nozzle operating conditions, since it is sufficient to know thrust at some one pressure $p_{к}$, in order to construct consumption characteristic. For the moment of entry of shock wave in the nozzle, for calculation of consumption characteristic there should be used formulas (III.55), (III.56), or (III.57), (III.58). Starting from the moment of entry of shock wave in the nozzle, thrust with decrease is illustrated by some curve, determined by regularities of shock wave motion and recovery pressure after the shock wave (zone I).

On Fig. IV.4 the dashed line plots change of thrust and specific thrust under the assumption of shock-free gas flow in the entire range of change of p_K. Intensity of decline of thrust and specific thrust of the engine with decrease of p_K at shock-free nozzle operating conditions are considerably greater than at conditions with shock wave. Decrease of intensity drop of thrust and specific thrust becomes clear from the following considerations.

Let us assume that at some pressure in the combustion chamber and ambient pressure in one case there could be realized gas flow conditions in the nozzle without shock wave, and in another – with shock wave. In the latter case thrust, taken from internal contour of combustion chamber, will be greater, since pressure affecting the nozzle wall after the shock wave will be greater than on the same part of the nozzle in case of shock-free (isentropic) gas flow in the nozzle. As a result, thrust and specific thrust are changed less intensively with decrease of pressure in the combustion chamber than in the case of realization of shock-free nozzle operating conditions in the entire range of change of pressure p_K.

It is necessary to emphasize that nozzle operating conditions with shock wave are useful only in separate cases with respect to the following considerations. If during engine operation the nozzle exit section area was changed in accordance with decrease of pressure in the combustion chamber (variable-area nozzle), then the consumption characteristic would flow more favorably than at nozzle operating conditions with shock wave. In view of great technical difficulties in creating a variable-area nozzle, it is necessary to use a fixed-area nozzle, pressure on the section of which is selected rather low with respect to ambient pressure for a number of rockets from the condition of obtaining the best characteristics on the average along the rocket path. In this case there can occur nozzle operating conditions with shock wave, and in this case conditions of isentropic flow in the nozzle, if they could be accomplished, would be less suitable than the operating conditions of a nozzle with shock wave. It is necessary to note that by using formulas (III.16) and (III.44) it is impossible to determine thrust and specific thrust in a vacuum according to the experiment, under conditions of which the nozzle operated with shock wave. In this case by these formulas we will obtain values of thrust and specific thrust, taken from the internal contour of the combustion chamber, characteristic only for concrete counterpressure, which have nothing to do with thrust and specific thrust in a vacuum, since in a vacuum there are no conditions for the appearance of shock wave in the nozzle. Fig. IV.5 shows the character of change of specific thrust, taken from internal contour, with change of pressure in the region of nozzle operation with shock wave. From this figure it is clear that specific thrust $P_{\text{уд. внутр}}$ is greater than specific thrust $P_{\text{уд. п}}$, i.e., than $P_{\text{уд. п}}$, which in reality is realized in a vacuum. For determination of specific thrust and thrust in a vacuum for combustion chambers, for which a shock wave enters in atmostpheric conditions, there are used special gas-dynamic installations, making it possible to create the necessary rarefaction in the nozzle region, excluding nozzle operation with shock wave.

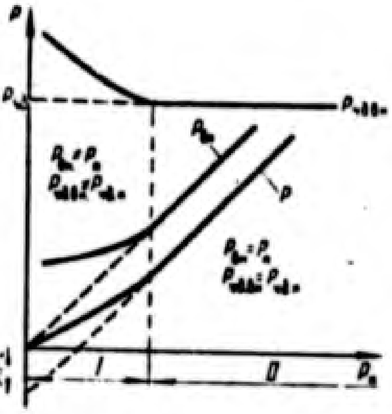

Fig. IV.5. Dependence $P_{\text{внутр}} = f(p_н)$ at assigned $p_к$=const.

The course of consumption characteristic is greatly affected by the selection of nozzle height or value of dimensionless area of nozzle f_c.

Figure IV.6 shows consumption characteristics of two identical engines, but with different dimensionless nozzle areas $f_{c_1} > f_{c_2}$. From the figure it is clear that thrust and specific thrust in the void of an engine with large dimensionless nozzle f_c area are higher at all combustion chamber pressures than for an engine with smaller value of f_c. Consumption characteristic (Fig. IV.7) during engine operation with some ambient pressure has a different character. At a certain pressure in the combustion chamber $p'_к$ thrust and specific thrust for

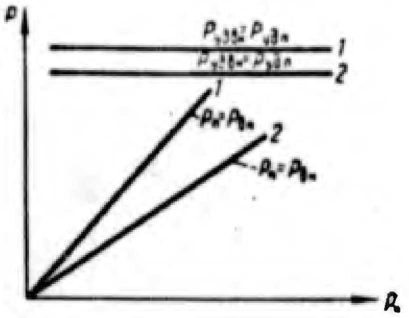

Fig. IV.6. Dependence of thrust and specific thrust of two combustion chambers on $p_к$ with $f_{c1} > f_{c2}$ when $p_0 = 0$.

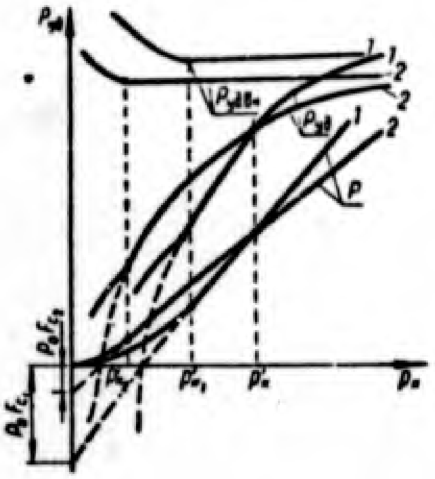

Fig. IV.7. Dependence of thrust and specific thrust of two combustion chambers at prescribed counterpressure.

the two engines are identical. With increase of pressure in the chamber above $p'_к$ thrust and specific thrust of the engine with f_{c_1} become larger than for an engine with f_{c_2}, and, conversely, with lowering of pressure in the combustion chamber below $p'_к$ characteristics of an engine with f_{c_2} become better. The last is explained by the known fact that the less the pressure on the nozzle section differs from ambient pressure, the better its basic characteristics will be — thrust and specific thrust. On Fig. IV.7 points $p'_{к_1}$ and $p'_{к_2}$ designate pressures of chamber with f_{c_1} and f_{c_2}, at which shock wave enters their nozzles. On Fig. IV.7 the dashed line plots values of thrust and specific thrust under the assumption that after pressure $p'_{к_1}$ and $p'_{к_2}$ there was realized isentropic gas flow in the nozzle.

Thrust control by the consumption characteristic is widely used in contemporary liquid-propellant rocket engines, but a great disadvantage of this method of control is decrease of specific thrust at all conditions besides rated. With increase of pressure above rated the specific thrust increases due to the smaller influence of static component $\frac{p_0F_c}{G}$. Both in overexpansion and underexpansion conditions the specific thrust of the combustion chamber is lower, with the exception of its rated operating conditions, than the possible value of specific thrust prescribed p_K and the calculated value of pressure on the nozzle section. Basic cause of decrease of specific thrust is nozzle operation in nonrated conditions. Furthermore, with fixed flow area of injectors (the most often used type) decrease of propellant consumption (pressure p_K) is accomplished by decrease of pressure drop at injectors, which leads to deterioration of the working process in the combustion chamber and additional decrease of specific thrust in the case of extreme control of liquid-propellant rocket engine thrust.

Figure IV.8 shows experimental consumption characteristic of a combustion chamber, obtained at altitude H = 0.6 and 30 km. From the figure it is clear that the combustion chamber has the greatest losses of thrust and specific thrust, as should have been expected, at H = 0 and minimum thrust conditions in view of the most deviation of nozzle operating conditions from rated deterioration of the working process in the chamber in connection with sharp decrease of pressure drop at the injectors. If at normal conditions specific thrust $P_{y\text{д}} \simeq 200$ kg·s/kg, then at minimum thrust conditions $P_{y\text{д}} \simeq 120$ kg·s/kg. On Fig. IV.8 the dashed line plots changes of specific thrust and thrust while neglecting shock wave in the nozzle, which show that at

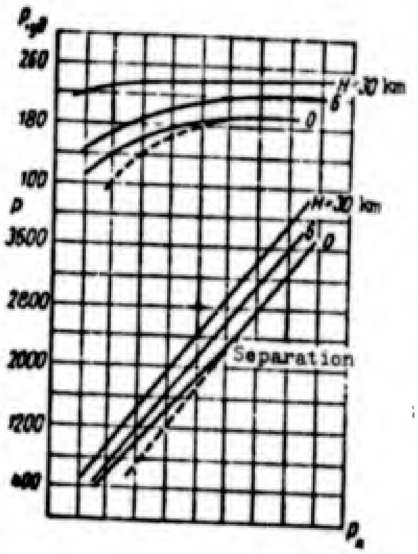

Fig. IV.8. Experimental consumption characteristic.

the indicated conditions the entry of shock wave into nozzle improves the liquid-propellant rocket engine characteristics.

Consequently, for decrease of specific thrust losses it is desirable to control the engine by consumption characteristic at the largest possible values of pressures in the combustion chamber, which is especially important for engines operating in a medium with high pressure. With decrease of counterpressure, its harmful effect on the course of consumption characteristic is reduced and specific thrust increases, and the flow of the consumption characteristic itself occurs smoother. Thus if on the ground (Fig. IV.8) the specific thrust at minimum thrust conditions is only 60% of specific thrust at normal conditions, then at an altitude of 30 km it increases to 92%.

The introduction of burning process at high pressures in the chamber with the prescribed range of thrust change is permitted, as in the case of decrease of ambient pressure, to improve the change of specific thrust with respect to consumption characteristic. Decrease of specific thrust with lowering of pressure in case of its increased initial values will occur smoother than at lower initial pressures in the combustion chamber.

From the preceding it is clear that ZhRD thrust control by the consumption characteristic is connected with greater or smaller specific thrust losses. These losses could have been excluded if with change of chamber thrust its nozzle always operated at rated conditions, and the quality of the working process remained constant.

The first requirement is satisfied when $\frac{p_к}{p_0} = \frac{p_к}{p_c}$. If p_0 = const, then pressure in the chamber should remain constant with change of thrust. These conditions can be fulfilled for a chamber, whose throat area is changed in direct proportion to the change of propellant consumption. This may be seen clearly from the expression for specific impulse of combustion chamber $p_к = \frac{G\beta}{F_{кр}}$.

For preservation of constant rated pressure on the nozzle section p_c it is necessary to have constant dimensionless nozzle area f_c, i.e., area of nozzle exit section should be changed in direct proportion to change of throat area.

It is extremely difficult to achieve a similar method of thrust control, in spite of all its advantages, because of the complexity of designing a nozzle capable of changing its geometric dimensions and reliably operating in a gas flow of high temperatures and velocities. Elimination or decrease of specific thrust losses, connected with deterioration of the working process because of decrease of pressure drop with decrease of propellant consumption, is possible for a single-chamber liquid-propellant rocket engine with the aid of variable-area injectors. In these injectors propellant consumption is reduced not by decrease of pressure drop at the injectors, but by change of area of the injector exit nozzle

$$G=\mu_{\Phi}F_{\Phi}\sqrt{2g\gamma\Delta p_{\Phi}},$$

where μ_{Φ} — discharge coefficient of injector; F_{Φ} — area of injector nozzle exit section; γ — specific gravity of liquid; Δp_{Φ} - pressure drop at injector.

Area of injector nozzle F_{Φ} should be changed in direct proportion to change of propellant consumption.

Figure IV.9 shows the consumption characteristic of an engine, for which relationship $\frac{F_c}{F_{кр}}=\text{const}$ could be achieved in the operating

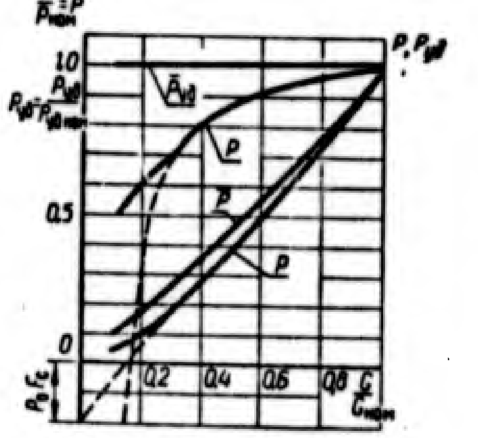

Fig. IV.9. Consumption characteristic when f_c = = const and $\frac{F_{\Phi}}{F_{кр}}=\text{const}$.

process and the quality of the working process would remain constant due to preservation of $\frac{F_\Phi}{F_{\text{кр}}}=\text{const}$. In view of the fact that with a similar method of control $p_{\text{к}}$ = const, the change of thrust and specific thrust on Fig. IV.9 is constructed as a function of propellant consumption.

For comparison there is plotted engine consumption characteristic at usual conditions, i.e., $F_c=\text{const}$, $F_{\text{кр}}=\text{const}$ and $F_\Phi=\text{const}$. From Fig. IV.9 it is clear that engine thrust control at $\frac{F_c}{F_{\text{кр}}}=\text{const}$ and $\frac{F_\Phi}{F_{\text{кр}}}=\text{const}$ occurs at constant specific thrust, whereas with the existing method of thrust control the value of specific thrust is sharply decreased with decrease of thrust. On Fig. IV.9 the subscript "ном" designates the value of thrust at normal conditions.

It is necessary to note that as yet there has not been achieved thrust control when $\frac{F_c}{F_{\text{кр}}}=f_c=\text{const}$ and $p_{\text{к}}=\text{const}$ because of technical difficulties. Attempts of designing variable-area injectors were made but they were not applied in view of their great structural complexity, time consumption in production and so forth.

For elimination of large specific thrust losses, appearing during liquid-propellant rocket engine operation with respect to consumption characteristic, multichamber liquid-propellant rocket engines are applied, for which thrust is changed not by lowering the pressure in combustion chambers, but by shutdown of separate chambers. In working combustion chambers there are maintained nominal and optimum parameters for a concrete liquid-propellant rocket engine, which permits achieving extreme thrust control without lowering the specific thrust.

In case it is not possible to attain the needed minimum thrust by shutdown of separate chambers, then further decrease of thrust is produced by decrease of propellant consumption in the remaining combustion chamber or remaining chambers. In this case the range of pressure change in the combustion chamber with prescribed thrust change will be smaller than in a single-chamber liquid-propellant rocket engine, and consequently, specific thrust losses will be smaller. A deficiency of a similar method of control is complication of design, lowering of operating reliability of the liquid-propellant rocket engine, and also the necessity of step thrust control.

Earlier it was noted that for a liquid-propellant rocket engine with pressurized fuel feed system, for liquid-propellant rocket engine with turbopump fuel feed system, operating on a closed cycle, in brief, for a liquid-propellant rocket engine, for which all the fuel is ejected into the environment in the form of combustion products only through the combustion chamber, characteristics of the combustion chamber are characteristics of liquid-propellant rocket engines. For liquid-propellant rocket engines, for which the fuel is ejected into the environment in the form of combustion products not only through the chamber, but also through other units, characteristics of the combustion chamber differ from that of liquid-propellant rocket engines. Such liquid-propellant rocket engines include ZhRD with turbopump fuel feed, for which the working medium of the turbine is ejected into the environment. Using, for example, equation of thrust (III.41) and specific thrust (III.42) for a liquid-propellant rocket engine, operating on open cycle with ejection of turbine working medium through the ejector pipes

$$P = P_{\text{к.с}} + P_{\text{р.сп}};$$

$$P_{\text{уд}} = P_{\text{уд.к.с}} \frac{1 + \frac{P_{\text{р.сп}}}{P_{\text{к.с}}}}{1 + \xi},$$

it is possible to construct consumption characteristic of liquid-propellant rocket engine.

During construction of the consumption characteristic for similar liquid-propellant rocket engines, the thrust and specific thrust of combustion chamber and ejector pipes are determined by the method discussed above. From calculation of turbopump unit we know gas flow rate to turbine and its pressure behind the turbine. As a result we can determine $P_{\text{р.сп}}$, ξ and values P and $P_{\text{уд}}$ of liquid-propellant rocket engine for each of its operating conditions. Figure IV.10 shows consumption characteristic of similar liquid-propellant rocket engines.

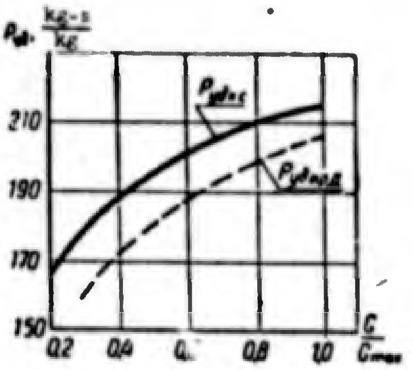

Fig. IV.10. Consumption characteristic of liquid-propellant rocket engine.

From Fig. IV.10 it is clear that specific thrust of the combustion chamber is greater than that of the liquid-propellant rocket engine. This is explained by the known fact that for a turbine there is necessary working medium with low temperatures from the condition of providing reliable operation of turbine blades. Therefore, propellant utilized for generation of working medium is burned at α, sharply different from optimum. As a result, some increase of thrust at the expense of ejector pipes is not compensated by raised propellant flow rate to turbine and term

$$\frac{1+\frac{P_{р.сп}}{P_{к.с}}}{1+\xi}$$

is always smaller than one. It is necessary to note that usually the propellant flow rate to turbine is reduced slower than flow rate to combustion chamber, owing to which the specific thrust of liquid-propellant rocket engine is not only smaller than specific thrust of the combustion chamber, but is also decreased more sharply with decrease of thrust than the specific thrust of the combustion chamber.

In conclusion one should note that the limits of thrust control by consumption characteristic are limited by the range of stable operation of the combustion chamber. Each combustion chamber has its range of change of pressure $p_к$, at which the process in the combustion chamber flows normally, stably. Deviation from permissible range of combustion chamber control with respect to pressure $p_к$ can lead to its destruction. Range of stable operation of the combustion chamber, operating by consumption characteristic, depends on numerous factors (type of propellant, combustion chamber design and others) and, as a rule, is determined experimentally.

§ 2. Altitude Performance

With change of ambient pressure there are changed basic parameters of liquid-propellant rocket engines — thrust and specific thrust. Character of their change from ambient pressure depends on a number of liquid-propellant rocket engine parameters. ZhRD parameters should be selected in such a way that performance of the ZhRD along the path of motion would be the most advantageous for the rocket, would assure it maximum range at prescribed weight or the prescribed range at minimum weight, i.e., would assure maximum terminal velocity at prescribed initial weight or the predetermined velocity at minimum initial rocket weight.

Dependence of thrust and specific thrust on ambient pressure received the name altitude performance because the first rockets were launched from the earth's surface and reached some flight altitude.

At present rockets are launched not only from the ground, but also underwater ("Polaris" missile") and then travel along the usual flight path, are launched from the atmosphere from some altitude into the water to various depths and so forth. Therefore, having left its traditional name as previous, we will examine change of ZhRD parameters not from flight altitude, but from ambient pressure. Moreover, in all the calculation formulas there enters ambient pressure, which affects liquid-propellant rocket engine characteristics.

Let us note that just as in the case of consumption characteristic, altitude performance of the combustion chamber will simultaneously be altitude performance of the liquid-propellant rocket engine, for which all the propellant fuel is ejected into the environment in the form of combustion products only through the combustion chambers (liquid-propellant rocket engine, operating on closed cycle and so forth).

For a liquid-propellant rocket engine with turbopump unit, for which part of the propellant is used for generation of turbine working medium with its subsequent ejection into the environment, altitude performance of the combustion chamber will differ from that of liquid-propellant rocket engine. The latter case will be examined at the end of the section.

Let us examine the course of altitude performance of liquid-propellant rocket engines taking into account the assumptions which were made earlier in examining the consumption characteristic. With isentropic conditions of gas flow in the nozzle the value of thrust and specific thrust is determined by equations

$$P = P_{\text{пустр}} - p_0 F_c,$$

$$P_{\text{уд}} = P_{\text{уд. пустр}} - \frac{p_0 F_c}{G}.$$

From the formulas it is clear that with increase of pressure p_0 the thrust and specific thrust are reduced linearly. At ratio $\frac{p_{\text{к}}}{p_0}$, determined for the given combustion chamber, a shock wave will enter the nozzle and thrust and specific thrust must be calculated by equations:

a) for small apex angles of nozzle

$$P = p_{\text{ск}} F_{\text{ск}} (1 + k M_{\text{ск}}^2) + p_{\text{ср}} (F_c - F_{\text{ск}}) - p_0 F_c;$$

$$P_{\text{уд}} = \frac{p_{\text{ск}} F_{\text{ск}} (1 + k M_{\text{ск}}^2)}{G} + p_{\text{ср}} \frac{(F_c - F_{\text{ск}})}{G} - \frac{p_0 F_c}{G};$$

b) for large apex angles of nozzle

$$P = p_{\text{сх}} F_{\text{сх}} (1 + k M_{\text{сх}}^2) - p_0 F_{\text{сх}};$$

$$P_{\text{уд}} = \frac{p_{\text{сх}} F_{\text{сх}} (1 + k M_{\text{сх}}^2)}{G} - \frac{p_0 F_{\text{сх}}}{G}.$$

Figure IV.11 shows change of basic engine parameters with change of counterpressure. As can be seen from the figure, the course of

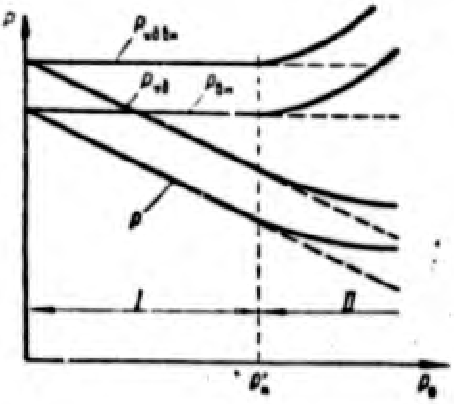

Fig. IV.II. Altitude performance of combustion chamber.

altitude performance of liquid-propellant rocket engine with change of ambient pressure can be divided into two sections: section of nozzle operation without shock wave I and section of nozzle operation with shock wave II.

On the section with isentropic (shock-free) nozzle operating conditions the thrust and specific thrust are decreased linearly with rise of ambient pressure. Specific thrust and thrust taken from the internal contour remain constant and are numerically equal to specific thrust and thrust in a vacuum.

In this case the working process in the chamber and its nozzle is autonomous from ambient pressure. At a certain pressure $p'_{\text{К}}$ the shock wave enters the nozzle of the chamber – linearity of change of thrust and specific thrust is disturbed. From the moment of entry of shock wave the thrust taken from internal contour $P_{\text{внутр}}$ of combustion chamber starts to increase and the intensity of decrease of ZhRD thrust with increase of pressure is reduced. Character of change of thrust and specific thrust at nozzle operating conditions with shock wave is determined by regularity of motion of shock wave into the nozzle depth and pressure recovery p_2 after the shock wave. On Fig. IV.11 dashed lines show the character of change of basic liquid-propellant rocket engine parameters in case the shock wave did not enter the nozzle and at all pressures p_0 in the nozzle there occurred isentropic gas expansion.

From Fig. IV.11 it is clear that from the moment of entry of shock wave in nozzle $P_{\text{внутр}} \neq P_{\text{п}} \neq \text{const}$ and $P_{\text{уд внутр}} \neq P_{\text{уд.п}}$, and is increased in proportion to penetration of shock wave into nozzle depth. Similar operating conditions are observed for ZhRD of the first step of intercontinental rockets, pressure on the nozzle section of which is selected rather low from conditions of obtaining mean maximum specific thrust on the powered-flight phase of the rocket or for rockets launched underwater ("Polaris" missile). For a similar type of rockets the engine parameters are selected from the condition of obtaining average maximum specific thrust on the air phase of the rocket, since the engine operates the most on this phase, and flight range is basically determined by engine parameters during operation outside the water trajectory. Therefore, for these rockets the pressure on nozzle section is obtained quite low ($P_c \cong 0{,}5$ at) and atmospheric pressure is sufficient, not yet indicating ambient pressures during rocket launch from underwater ($p_0 \cong 10$ [atm(abs.)]), so that the shock wave would enter the nozzle depth. From Fig. IV.11 it is clear that in the shown conditions the nozzle operating conditions with shock wave improves liquid-propellant rocket engine characteristics.

It is necessary to note that according to the results of ground tests with the presence of shock wave it is impossible to calculate specific thrust and thrust in a vacuum by usual formulas, since in this case there will be determined thrust and specific thrust not in a vacuum, but that taken from the internal contour of combustion chamber at concrete counterpressure, which will be greater than thrust and specific thrust in a vacuum.

For determination of thrust and specific thrust in a vacuum similar engines are tested on special stands, in which there is created the necessary rarefaction about the nozzle, excluding its operation with shock wave.

Let us consider how the course of altitude performance is changed with change of pressure $p_к$ in the same engine (f_c = const) in case of isentropic gas flow in the nozzle.

The lower the pressure on the nozzle section, the greater the thrust and specific thrust on the ground differs from that in a vacuum. Thus, for example, for liquid-propellant rocket engine of the second stage of a "Titan" rocket the thrust on the ground and in a vacuum equals P = 30.4 t, $P_{\text{внут}} = P_{п} =$ 36.6 t respectively, i.e., is increased approximately 20%.

Let us assume that at the second conditions pressure in the combustion chamber is two times greater, i.e., $p_{к_2} = 2p_{к_1}$ or $G_2 = 2G_1$, then

$$P_2 = 2P_{\text{внутр. }1} - F_c P_0,\quad P_{\text{уд. }2} = P_{\text{уд. внутр}} - \frac{p_0 F_c}{2G_1};$$

$$P_1 = P_{\text{внутр. }1} - F_c P_c,\quad P_{\text{уд. }1} = P_{\text{уд. внутр.}} - \frac{p_0 F_c}{G_1}.$$

Since specific thrust taken from the internal contour does not depend on pressure in the chamber, let us designate

$$P_{\text{уд. внутр}} = P_{\text{уд. внутр }2} = P_{\text{уд. внутр}}.$$

From the given dependences it is clear that with increase of pressure in the combustion chamber the effect of ambient pressure is reduced. In the limit, $p_к$ approaches an infinitely large value $P_{уд} \to P_{\text{уд. внутр}}$. From this point of view it is advantageous to produce the process of propellant combustion at the greatest possible pressure $p_к$.

Figure IV.12 shows dependence of change of thrust, specific thrust $P_{\text{внутр}}$, $P_{\text{уд.внутр}}$, P, $P_{\text{уд}}$ on ambient pressure for an engine with various pressures in the combustion chamber. On Fig. IV.12 it is clear that specific thrust for liquid-propellant rocket engine with large pressure in the combustion chamber is changed smoother with change of ambient pressure and is larger in absolute value as compared to liquid-propellant rocket engine with less pressure in the combustion chamber. The latter is explained by the smaller influence of ambient pressure at higher pressures in the combustion chamber.

Fig. IV.12. Altitude performance of combustion chambers at various values of combustion chamber pressure.

Further, let us consider how the altitude performance of three liquid-propellant rocket engines will be changed, for which all the parameters are identical with the exception of dimensionless area of nozzle f_c.

Let us assume $f_{c1}>f_{c2}>f_{c3}$, i.e., $p_{c1}<p_{c2}<p_{c3}$. Consequently, nozzles operate in rated conditions at different counterpressures (altitudes) Figure IV.13 shows character of change of specific thrust of these

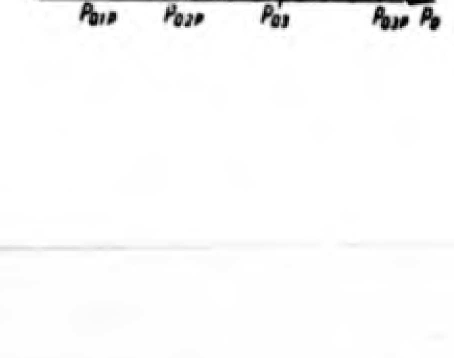

Fig. IV.13. Altitude performance of combustion chambers when $p_{\text{к}}=\text{const}$ and $f_{c1}>f_{c2}>f_{c3}$.

liquid-propellant rocket engines with change of ambient pressure.

In a certain scale the change of thrust of these liquid-propellant rocket engines occurs analogously. From Fig. IV.13 it is clear that at the calculated counterpressure each liquid-propellant rocket engine gains in specific thrust as compared to other liquid-propellant rocket engines. For example, engine nozzle f_{c3} operates at rated conditions at p_{01p} and has large specific thrust, since nozzles of the other two liquid-propellant rocket engines operate with overexpansion. Liquid-propellant rocket engine with nozzle f_{c2} has large specific thrust when $p_0 = p_{02p}$, since the ZhRD with nozzle f_{c3} operates at underexpansion conditions, and the ZhRD with nozzle f_{c1} – at overexpansion conditions. Nozzle f_{c1} has the greatest overexpansion and at a certain pressure a shock wave enters it. On Fig. IV.13 a dashed line shows change of specific thrust of a liquid-propellant rocket engine with nozzle under the assumption of isentropic outflow of gas in it. From Fig. IV.13 it is clear that the less the rated pressure on the nozzle section, the steeper is the dependence of specific thrust with change of ambient pressure. Consequently, it is desirable to use each of the nozzles in the zone of ambient pressures (altitudes) close to the rated pressure on the nozzle section. An ideal case would be to have a variable-area nozzle, permitting change of pressure on the nozzle section in accordance with change of ambient pressure. For example, during ascent the ambient pressure is decreased, then for maintaining the rated nozzle operating conditions it is necessary to increase the area of nozzle exit section F_c. On Fig. IV.13 a dashed line shows the course of altitude performance with a variable-area nozzle $P_{\text{уд.р}}$.

Creation of a variable-area nozzle would be especially important concerning increase of specific thrust of ZhRD and on this basis the improvement of basic rocket characteristics (weight, dimensions, range and so forth).

At present when variable-area nozzles are not as yet created, pressure on the fixed-area nozzle section is selected from condition of obtaining maximum average specific thrust along the rocket path.

In the conclusion of the section let us indicate the specific character of calculation of altitude performance of a liquid-propellant rocket engine, for which part of the propellant is ejected in the form of combustion products not only through the ZhRD combustion chamber, but also, for example, through the turbopump unit turbine.

In this case, by using equation

$$P = P_{\text{к.с}} + P_{\text{р.вп}}$$

and

$$P_{\text{уд}}^{\cdot} = P_{\text{уд.к.с}} \frac{1 + \frac{P_{\text{р.вп}}}{P_{\text{к.с}}}}{1 + \varepsilon},$$

we construct dependence of change of both combustion chamber thrust and thrust of ejector exhaust pipes depending on ambient pressure by the discussed method of calculation of altitude performance of combustion chamber. In this case, as with consumption characteristic, specific thrust of ZhRD will be lower than that of the combustion chamber by value $\frac{1 + \frac{P_{\text{р.вп}}}{P_{\text{к.с}}}}{1 + \varepsilon}$.

CHAPTER V

LIQUID-PROPELLANT ROCKET ENGINE PROPELLANTS

In contemporary liquid-propellant rocket engines as the energy source there is used energy of the chemical reaction of liquid propellant combustion and as working medium – combustion products of this propellant.

The concept of rocket propellant includes both the energy source and the working medium itself.

§ 1. Energy Sources and Working Medium for Rocket Engines

As possible chemical[1] sources of energy for jet engines there can be considered: energy of association (recombination) of molecules dissociated into atoms or radicals; energy of oxidizing processes; energy of oxidizing processes; disintegration energy of unstable compounds.

Let us consider each of the possible energy sources.

Energy of association of atoms and radicals into molecules. Dissociation of molecules of certain gases (hydrogen, nitrogen, oxygen, methane) occurs with absorption of a large amount of energy.

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[1] Other possible energy sources for rocket engines (nuclear, electrical and others) are not considered in this training aid.

Energy absorbed during dissociation is separated during association (combination) of atoms or radicals into molecules. Energy release in 1 kg of dissociated gas will comprise: for hydrogen 51,620 kcal, for ammonia 19,800 kcal, for nitrogen 8030 kcal, for oxygen 3660 kcal, for methane 6300 kcal, and for water 6560 kcal. Energy content of molecules dissociated into atoms and radicals considerably exceeds the energy release of combustion reactions used at present.

High energy data of these reactions are combined with high values of gas constants of end products (especially for hydrogen $R = 424 \frac{kg \cdot m}{kg°C}$).

It is necessary, of course, to consider that at high temperatures, which will be developed with these reactions, part of the molecules will again dissociate into atoms and radicals with absorption of energy, until equilibrium is established, corresponding to given temperature and pressure conditions.

Application of association of atoms and radicals into molecules in the liquid-propellant rocket engine will become possible only after development of methods of their stabilization[1] in normal conditions.

Energy of oxidizing processes. Oxidizing processes – combustion reactions, are the most widely applied as sources of energy for liquid-propellant rocket engines.

Combustion reactions, although inferior to the above-mentioned sources, nevertheless ensure sufficiently high heat release.

Thus, for example, during combustion of kerosene in oxygen of 1 kg of propellant mixture there is released 2350 kcal. Contemporary chemistry has available more caloric propellant mixtures.

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[1] "Lifetime" of free atoms and radicals is characterized by values around 10^{-6} s.

The various physicochemical composition of parent fuels and their combustion products permits widely using this energy source for the most diverse (in size and purpose) flight vehicles. Theoretically with the use of energy of oxidizing processes the possible specific thrusts can reach 500 kg·s/kg.

Disintegration energy of unstable compounds. Contemporary chemistry has available a number of chemical compounds, which are able with the presence of external pulses (thermal, shock) or catalysts to be decomposed with energy release into simpler, thermodynamically stabler substances. Such compounds include mainly substances of endothermic origin and some unstable substances of exothermic origin.[1]

Of the endothermic compounds are the richest energies acetylene (C_2H_2 - heat of formation of elements is equal to +54.19 kcal/mole) and hydrazoic acid (HN_3 - heat of formation of elements is equal to +67.00 kcal/mole).

Disintegration of these compounds occurs according to equations:

$$C_2H_2 \longrightarrow 2C + H_2 + 54.19 \text{ kcal/mole;}$$

$$HN_3 \longrightarrow 1{,}5N_2 + 0{,}5H_2 + 67.0 \text{ kcal/mole.}$$

The amount of released energy converted to 1 kg will be: for acetylene 2084 kcal, for hydrazoic acid 1592 kcal.

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[1] Compounds, obtained from elements are accompanied by energy absorption is called endothermic. Compounds, obtaining from elements which are accompanied by energy release, are called exothermic.

It is necessary to consider that in thermochemistry (in contrast to thermodynamics) a positive thermal effect, heat release is considered a positive thermal effect, and heat absorption – negative. Therefore, in thermochemical and thermodynamic reference books the heats of formation have opposite signs (with equality of absolute values). In this aid the heats of formation have signs reflecting the thermodynamic understanding of the process.

Exothermic substances of this group include hydrogen peroxide (H_2O_2, heat of formation of which from elements H_2 and O_2 – 44.84 kcal/mole) – compound in pure form is sufficiently stable, but under the influence of different catalysts is decomposed with energy release into stabler substances: water and oxygen. Energy of decomposition of 100% hydrogen peroxide is 12.957 kcal/mole or converted to 1 kg – 381 kcal/kg.

Effectiveness of ZhRD operation, all other conditions being equal, is determined by exhaust velocity of combustion products (working medium), depending on combustion temperature, gas constant and index of expansion process, which in turn depend on strength of energy source and quality of working medium.

Quality of working medium is characterized by value of specific gas constant $R = \frac{848}{\mu}$, where μ – average molecular weight of working medium, and by value of polytropic index of expansion – n. The higher the value of specific gas constant, the higher the (other things being equal) exit velocity is. From this point of view the products, being of interest for liquid-propellant rocket engine, can be arranged (in order of decrease of value of specific gas constant) in the following series:

$$H_2\left(R = 424\frac{\text{kg-m}}{\text{kg}^\circ\text{C}}\right);\ He\left(R = 212\frac{\text{kg-m}}{\text{kg}^\circ\text{C}}\right);\ H_2O\left(R = 47.1\frac{\text{kg-m}}{\text{kg}^\circ\text{C}}\right);$$

$$HF\left(R = 42.4\frac{\text{kg-m}}{\text{kg}^\circ\text{C}}\right);$$

$$BeO\left(R = 33.9\frac{\text{kg-m}}{\text{kg}^\circ\text{C}}\right);\ LiF\left(R = 32.6\frac{\text{kg-m}}{\text{kg}^\circ\text{C}}\right);$$

$$N_2\left(R = 30.3\frac{\text{kg-m}}{\text{kg}^\circ\text{C}}\right);\ CO\left(R = 30.3\frac{\text{kg-m}}{\text{kg}^\circ\text{C}}\right);$$

$$Li_2\left(R = 28.3\frac{\text{kg-m}}{\text{kg}^\circ\text{C}}\right);\ O_2\left(R = 26.5\frac{\text{kg-m}}{\text{kg}^\circ\text{C}}\right);$$

$$MgO\left(R = 21.2\frac{\text{kg-m}}{\text{kg}^\circ\text{C}}\right);CO_2\left(R = 19.3\frac{\text{kg-m}}{\text{kg}^\circ\text{C}}\right);$$

$$BeF_2\left(R = 18.05\frac{\text{kg-m}}{\text{kg}^\circ\text{C}}\right);SiO_2\left(R = 14.1\frac{\text{kg-m}}{\text{kg}^\circ\text{C}}\right);$$

$$AlF_3\left(R = 10.2\frac{\text{kg-m}}{\text{kg}^\circ\text{C}}\right);\ CF_4\left(R = 9.63\frac{\text{kg-m}}{\text{kg}^\circ\text{C}}\right).$$

In the given series there are substances with high boiling temperatures (metal oxides, silicon oxide). These substances are included in the table for comparison under the assumption that in the liquid-propellant rocket engine chamber the temperature will be kept higher than the boiling point of these substances at corresponding pressures. Polytropic index of $n = (c_p/c_v)$ depends on the number of atoms in a gas molecule. The biggest value of n is reached for monatomic gases. With increase of number of atoms in a molecule n is decreased, which leads to deceleration of outflow.

Thus, the highest exit velocity can be obtained when using working media consisting of light (with low molecular weight) low-atomic molecules.

§ 2. Classification of Rocket Propellants

It is possible to classify rocket propellants by proceeding from the state of matter of propellant components and the method of use of propellant in the rocket engine. By this criterion rocket propellants are divided into:

1) solid rocket propellants (propellant powders);

2) monopropellants;

3) propellants of separate supply;

4) blended propellants.

Solid rocket propellants.

Advantages of solid rocket propellants are simplicity of construction of the engine for them, constant readiness for use, and possibility of prolonged storage in the object.

Disadvantages of these propellants are comparatively low specific thrust and high weight of engine construction; difficulties of engine thrust control and restarting; considerable change of combustion rate with change of initial temperature of propellant.

In view of their specific features (accomodation of the entire propellant supply inside the combustion chamber, absence of feed systems and others) solid rocket propellants are separated into an independent area of technology and are not examined in this aid.

Liquid (monopropellants). These propellants are either individual liquid substances, able to release energy during decomposition with the formation of gaseous products, or blends (solutions, emulsions, suspensions) of combustible with oxidizers in the necessary ratios for burning. The propellant in this case is placed in one tank and is fed to combustion chamber through injectors.

Advantage of this class of propellants is simplification of engine construction.

Disadvantages of monopropellants are limitation of calorific value, connected with rise of explosive properties in proportion to its increase; danger of application of propellant for cooling the combustion chamber.

Propellants with separately fed components. This class of propellants is distinguished by the fact that propellant components (fuel and oxidizer) are stored in separate tanks and are fed to the combustion chamber separately, where their mixing occurs.

These propellants at present permit obtaining the greatest (within limits of possibility of chemical sources of energy) specific thrusts, accomplishing thrust control, restarting of engine in flight and so forth.

A disadvantage of this class of propellants is the intricate construction of the propulsion system with a large amount of components and subassemblies, and with an intricate control and regulating system.

Blended propellants. In these propellants, as in separately fed, oxidizer and fuel are stored separately and are mixed only in the combustion chamber. With use of blended propellants only one component is fed to the combustion chamber in liquid state. The other component (similar to solid propellants) is placed in the combustion chamber in the form of a solid charge. Blended propellants combine the advantages of separately fed propellants, monopropellants and solid propellants. For example, the specific gravity of blended propellants can be on the level of solid propellants, i.e., substantially higher than for separately fed propellants. With respect to weight characteristics of propulsion systems the blended propellants occupy an intermediate position between separately fed and solid rocket propellants. Therefore, blended propellants can be of interest for certain types of rockets. These propellants are not examined in this training aid.

The field of application of each class of rocket propellants is determined by its specific peculiarities and the concrete operating conditions of some flight vehicle.

Propellant oxidizers. Substances or mixtures of substances, containing a predominant quantity of oxidizing elements (O, F, Cl, and others[1]) are called propellant oxidizers. Propellant oxidizers can be O_2, O_3, F_2, OF_2, NF_3, CIF_3, HNO_3, N_2O_4, $C(NO_2)_4$, H_2O_2, and others.

Propellant fuels. Substances or mixtures of substances, containing a predominant quantity of combustible elements (H, C, Li, B, Be, Al, Mg, and others) are called propellant fuels. Propellant fuels can be hydrocarbons (C_nH_m), amines, hydrazines, pyridines ($C_nH_mN_k$), alcohols, ethers ($C_nH_mO_k$), nitro compoinds ($C_nH_m(NO_2)_k$), metals hydrides (LiH, $LiBH_4$, B_5H_9), and others.

If fuels or oxidizer consist of a mixture of several individual chemical substances, then each separate substance is named a fuel or oxidizer component.

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[1] In certain cases the oxidizing agent can be nitrogen, for example, as in the reaction of boron hydrides with containing nitrogen compounds $2B_5H_9 + 5N_2H_4 \rightarrow 10BN + 19H_2$.

Basic requirements for propellant, determined by theory of rocket flight, are reduced to the following:

1) maximum specific thrust (exit velocity);

2) maximum specific gravity.

Besides this, requirements are imposed on propellants, which are caused by its specific operating conditions in the engine and on the rocket.

Feed of large quantities of propellant components to the combustion chamber of a liquid-propellant rocket engine is possible only if they are in tanks in liquid state, therefore propellant should be liquid in the entire temperature range of operation of the rocket, for example ±50°C.

Propellant components utilized for cooling the combustion chamber must satisfy the following basic requirements:

1) have high value of heat capacity;

2) high boiling point;

3) high value of heat of evaporation;

4) have thermal stability, and have no coke formation and gumming in the cooling jacket during contact with the heated combustion chamber wall.

Propellant entering the combustion chamber should ignite easily and burn rapidly, therefore it should have: 1) low ignition temperature; 2) small ignition delay; 3) high burning rates.

Storage, transfer and shipping of propellant components introduce additional requirements for propellant; it should be:

1) chemically and physically stable during prolonged storage;

2) little-corrosive to structural materials;

3) nontoxic (desirable quality);

4) explosionproof.

Furthermore, general requirements are imposed on propellant.

1. Provision of raw material and industrial basis.

2. Accessibility.

3. Low cost.

Naturally, it is impossible to fully satisfy all the enumerated requirements simultaneously. Therefore, during comparative appraisal of various propellants it is necessary to examine their properties in a group, first of all from the point of view of satisfaction of basic requirements and operational requirements of the rocket.

§ 3. Propellant Oxidizers

Selection of oxidizer for a liquid-propellant rocket engine is guided by the same requirements that are imposed on propellant on the whole.

For maximum use of chemcial energy the liquid-propellant rocket engines operate at propellant component ratios close to stoichimetric.

With this, the quantity of oxidizer exceeds that of fuel (by weight) 2-6 times, i.e., weight of oxidizer is 2/3 to 6/7 the weight of the entire propellant.

In contemporary rockets the weight of propellant is about 90% of the total weight of the propulsion system, consequently, up to 85% of the entire weight of the propulsion system is necessary. This circumstance causes one to approach the selection of oxidizer for liquid-propellant rocket engines especially attentively.

Comparative evaluation of energy qualities of oxidizers is accomplished by the value of specific thrust of propellants on the basis of comparable oxidizers and by the specific gravity of these propellants.

For an objective appraisal the comparison is performed separately for low-boiling (cryogenic) and high-boiling oxidizers.

A separate evaluation is expedient because during the use of liquified gases it is necessary to encounter a number of difficulties, overcoming which can be justified only under condition of obtaining an essential increase of specific thrust and flight range of the rocket vehicle as compared to high-boiling oxidizers.

For evaluation of the qualities of some oxidizer the comparison is performed with the most accessible oxidizers, those already used in rocket technology: low-boiling – with liquid oxygen, high-boiling – with nitric acid or oxidizers in its base.

Low-boiling oxidizers include those with a critical temperature lower than the upper limit of the operational temperature range (lower than +50°C). Of the low-boiling oxidizers at present liquid oxygen has received practical application in series objects. Liquid fluorine and fluorine monooxide are in the experimental investigation stage. Such oxidizers as nitrogen trifluoride NF_3 tetrahydroxyfluoride N_2F_4 and ozone O_3, which possess certain qualities (high specific gragity NF_3 and high energy data O_3) and which are of interest for use in liquid-propellant rocket engines, if not in pure form, then in the form of mixtures with other oxidizers, have not yet emerged from the laboratory investigation stage.

High-boiling oxidizers include those for which the critical temperature is above +50°C, i.e., substances which can be transported and stored in liquid state in sealed tanks under low excess pressure.

Of the high-boiling oxidizers, mixtures of nitric acid with nitrogen tetroxide, nitrogen tetroxide N_2O_4 and hydrogen peroxide H_2O_2 are widely applied. In the final stage there is found chlorine trifluoride ClF_3. There are conducted laboratory investigations of such oxidizers as tetranitromethane $C(NO_2)_4$, perchloryl fluoride $(FClO_3)$. The possibilities of application of chloric acid $(HClO_4)$ are analyzed.

Basic physicochemical characteristics of low-boiling and high-boiling oxidizers are listed in Table V.1.

Table V.1.

Designation of oxidizer	Chemical formula	Molecular weight	Boiling point	Freezing point	Specific gravity
		M	°C	°C	g/cm³
Nitric acid	HNO_3	63	+86,0°	— 41,2	1,52
Tetranitromethane	$C(NO_2)_4$	196	+126	+ 13,8	1,65
Nitrogen tetroxide	N_2O_4	92	+21,3	— 11,23	1,45
Perchloric acid	$HClO_4$	100,5	+110,0	— 112,0	1,78
Hydrogen peroxide	H_2O_2	34	+150,2	— 0,461	1,44
Chlorine trifluoride	ClF_3	92,5	+12,1	— 82,6	1,77 $t_{кип}$
Oxygen	O_2	32	—182,96	—218,4	1,14 $t_{кип}$
Ozone	O_3	48	—111,9°	—251,5	1,46 $t_{кип}$
Fluorine	F_2	38	—187,99°	—218,8	1,51 $t_{кип}$
Oxygen fluoride	OF_2	54	—144,8	—223,8	1,53 $t_{кип}$

Low-Boiling Oxidizers

Liquid oxygen (O_2). Oxygen is obtained from the air by successive liquefaction and separation in liquid form from nitrogen and other gases, which the composition of the earth's atmosphere.

Dependences of specific gravity, vapor tension, viscosity and thermal conductivity of liquid oxygen on temperature are shown in Figures V.1-V.4.

Pure oxygen does not explode in either gaseous or liquid states. However, mixtures of it with small quantites of combustible substances are able to explode from even very weak pulses (compression, friction, electrification during flow along pipelines and others). Therefore, tanks, pipelines and fittings for both liquid and gaseous oxygen must be thoroughly degreased by dichlorethane, ethyl aclohol or other volatile solvents.

Industry produces two types of liquid oxygen.

They differ by oxygen content: from 99.2% by volume to 98.5%. Acetylene content should not exceed 0.3 cm^3/ℓ.

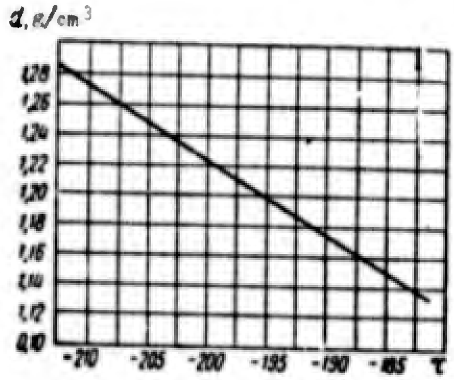

Fig. V.1.

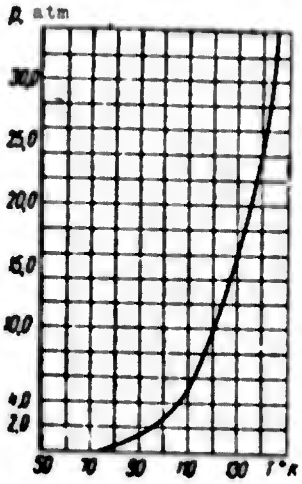

Fig. V.2.

Fig. V.1. Dependence of specific gravity of liquid oxygen on temperature.

Fig. V.2. Dependence of vapor tension of oxygen on temperature.

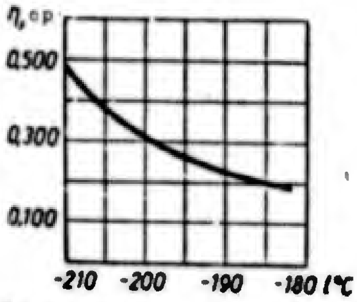

Fig. V.3.

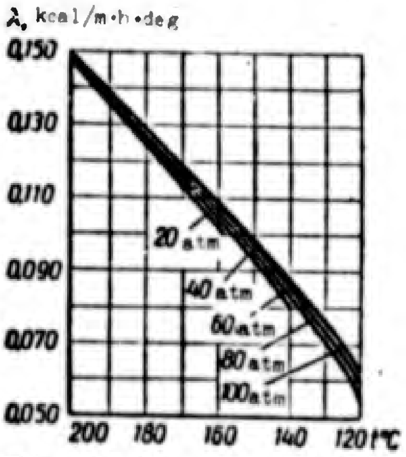

Fig. V.4.

Fig. V.3. Dependence of viscosity of liquid oxygen on temperature.

Fig. V.4. Dependence of coefficient of thermal conductivity of liquid oxygen on temperature and pressure.

For decrease of losses liquid oxygen is stored and transported in a special heat-insulated container.

Various metals behave differently at the temperature of liquid oxygen. Such metals as copper, brass, aluminum and its alloys and alloyed steels of type 1Kh19N9T practically do not change their properties and can be used for the manufacture of tanks, pipelines and fittings under liquid oxygen. "Ferrous" metals lose ductility and become very brittle, although their tensile strength increases in the process.

As packing materials in equipment for liquid oxygen there are used materials with insignificantly changing elasticity at low temperature, namely asbestos-rubber cement (paronite), degreased leather, copper, aluminum and lead and others.

<u>Liquid ozone</u> O_3. Ozone is an allotropic modification of oxygen with three atoms per molecule.

Dependences of specific gravity and vapor tension of ozone on temperatures are presented in Figs. V.5 and V.6.

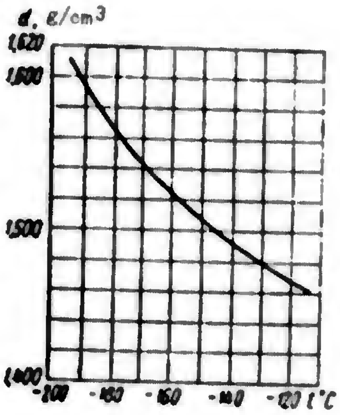

Fig. V.5.

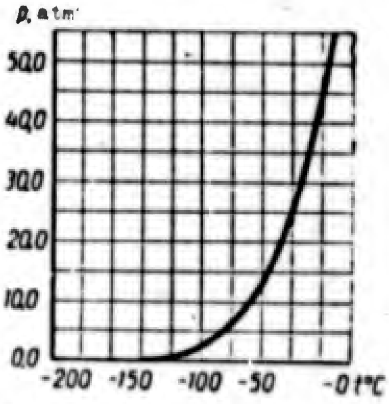

Fig. V.6.

Fig. V.5. Dependence of specific gravity of liquid ozone on temperature.

Fig. V.6. Dependence of vapor tension of ozone on temperature.

Ozone in gaseous state has an azure color, in liquid-dark-blue.

Ozone is an unstable substance, inclined toward explosive decomposition under the influence of external pulses, where this inclination increases with the presence of various impurities. Explosion sensitivity is reduced in proportion to dilution of ozone by oxygen, in which it is dissolved well. However, complete mutual solubility in oxygen is reached only at -153°C. At lower temperatures there occurs stratification of solutions. Due to the large difference of boiling temperatures of ozone (-112°C) and oxygen (-183°C), during storage such solutions must be enriched by a high-boiling component (ozone) and stratified with the formation of a lower layer with a high (∿70%) concentration of ozone, very explosion sensitive.

Ozone possesses high chemical activity. Many organic substances self-ignite upon contact with it. All metals (except gold, platinum and iridium) are rapidly oxidized with ozone.

Ozone belongs to highly toxic substances. Its maximum permissible content in air is 0.0001 mg/ℓ.

Liquid fluorine F_2. Fluorine in the form of compounds is widely spread in nature. Raw materials for producing fluorine are fluorspar KHF_2 and fluorite CaF_2.

Dependences of specific gravity and vapor tension of liquid fluorine are shown in Figs. V.7 and V.8.

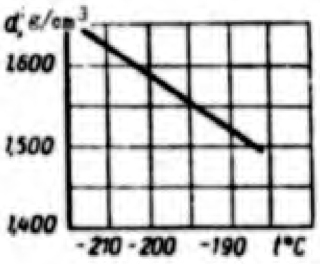

Fig. V.7. Dependence of specific gravity of liquid fluorine on temperature.

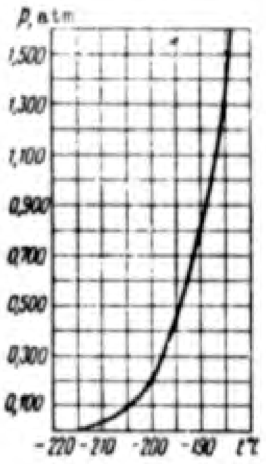

Fig. V.8. Dependence of vapor tension of liquid fluorine on temperature.

Gaseous fluorine is pale-yellow in color. In liquid state fluorine is bright-yellow in color.

Fluorine is the most active oxidizing element. Most substances actively interact with fluorine. While interacting with oxides, fluorine displaces oxygen and transforms oxides into fluorides.

Steel and copper pipelines under the action of gaseous fluorine are coated inside with a thin, but rather durable film of metal fluoride, preventing its further destruction. Traces of oil or other organic substances inside the pipeline lead to warming up and burnout. With the presence of bends in the pipelines the forming film of metal fluoride cracks and carries away the flow of fluorine in the form of powder. This explains the especially high erosional effect of fluorine on metals in places where the direction of flow motion sharply changes (bends of pipelines, gates, valves, etc.). Monel-metal and nickel are the least subject to the erosional action of fluorine. These metals can be recommended for the manufacture of pipelines, gates and valves. Copper and aluminum, which can be used for a number of structural elements of liquid-propellant rocket engines, react slower than others with fluorine.

Of the elastic packing materials there can be recommended fluoroplastic-teflon.

Fluorine is a highly toxic substance. Maximum permissible concentration of fluorine in air is 0.0001%.

With use of fluorine as rocket propellant oxidizers it is also necessary to consider the high aggressiveness and toxicity of hydrogen fluoride, forming during combustion.

Oxygen fluoride OF_2. Oxygen fluoride, or fluorine monooxide, is the stablest compound of oxygen with fluorine.

In liquid state it is bright-yellow in liquid. Oxygen fluoride is similar in chemical activity to ozone (less active than fluorine). Dry oxygen fluoride is a stable compound – is not decomposed with heating above +100°C. Mixtures of oxygen fluoride with steam detonate.

With respect to toxicity oxygen fluoride is not inferior to fluorine, however the high (as compared to oxygen) boiling point of oxygen fluoride permits storing it under conditions of cooling by liquid oxygen under low pressure in hermetically sealed tanks, which essentially facilitates the use and transportation of oxygen fluoride.

In combustion products of propellants based on oxygen fluoride there is contained a considerable amount of hydrogen fluoride. Therefore, the application of this oxidizer requires the same measures of protection from aggressive and toxic exhaust gases as in the case of fluorine.

Besides those described above, at present there are considered low-boiling rocket propellant oxidizers – nitrogen fluoride compound: nitrogen trifluoride NF_3 and tetrahydroxyfluoride N_2F_4. Both these compounds are sufficiently stable substances with boiling temperatures (-119°C) for NF_3 and (-74°C) for N_2F_4. In mixtures with other low-boiling oxidizers in certain cases their application can be expedient.

High-Boiling Oxidizers

Nitric acid HNO_3. Nitric acid with the addition of nitrogen tetroxide is widely used in contemporary rocket technology.

Mass production, accessibility and inexspensiveness of nitric

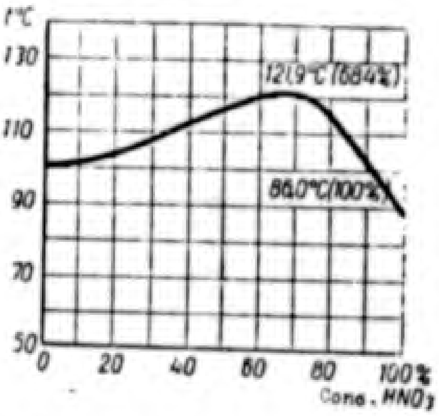

Fig. V.9.

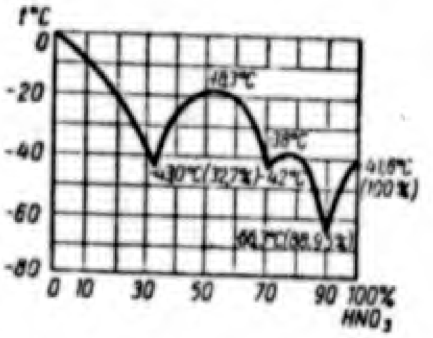

Fig. V.10.

Fig. V. 9. Dependence of boiling point of aqueous solutions of nitric acid on concentration.

Fig. V.10. Dependence of freezing point of nitric acid solutions on concentration.

acid were the basic reasons of its introduction to rocket technology, in spite of a number of essential negative qualities.

Data in Table V.1 pertain to 100% nitric acid, which is a colorless, heavy, mobile liquid, highly fuming in air. During storage it is light-yellow in color, since as a result of decomposition of nitric acid there will be formed nitrogen dioxide, which gives a yellow color to nitric acid.

The tendency to decomposition and high hygroscopicity do not permit producing 100% nitric acid in industrial scales. In rocket technology there is used nitric acid of not less than 98% concentration. A small quantity of water essentially affects the physicochemical characteristics of nitric acid, shown in Figs. V.9-V.14.

Nitric acid of any concentrations is not an explosive. Mixtures of concentrated nitric acid with combustibles are able to explode under the influence of external pulses, and in certain cases as a result of exothermic reactions, occurring between nitric acid and fuel.

Nitric acid mixes well with nitrogen tetroxide. Such solutions with various nitrogen tetroxide content have the better physicochemical properties than pure nitric acid, and are widely applied in

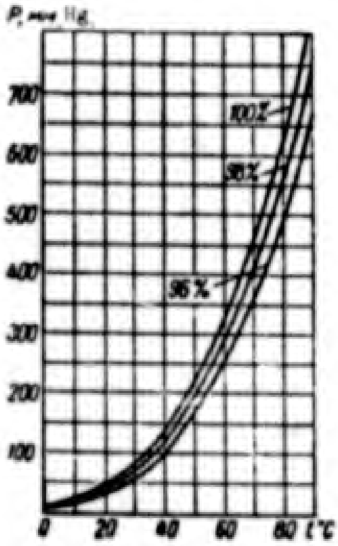

Fig. V.11.

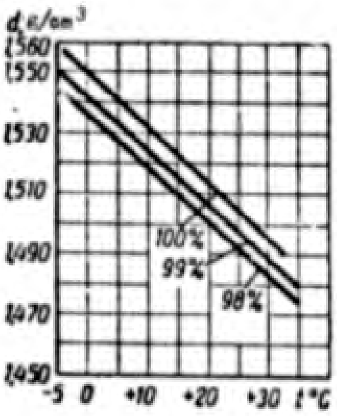

Fig. V.12.

Fig. V.11. Dependence of vapor tensions of aqueous solutions of nitric acid on concentration and temperature.

Fig. V. 12. Dependence of specific gravity of aqueous solutions of nitric acid on temperature and concentration.

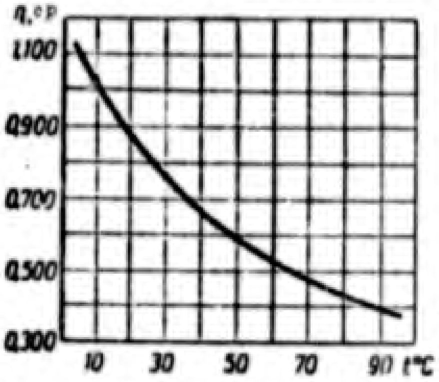

Fig. V.13.

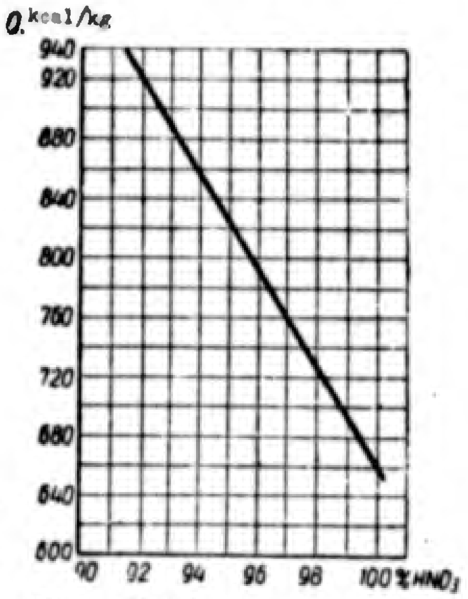

Fig. V.14.

Fig. V.13. Dependence of viscosity of nitric acid (conc. 99.51%) on temperature.

Fig. V.14. Dependence of heat of formation of nitric acid on concentration (taking heat of dissolution and heat of formation of water into account).

rocket technology.

Nitric acid possesses high corrosivity. Therefore, the selection of structural materials for nitric acid is limited by aluminum and high-alloy chromium and chromium-nickel steels. At temperatures of +50°C and higher corrosion of the shown steels in 98-99% nitric acid increases so much that they should pertain to the category "low stable" and "unstable."

Corrosion activity of nitric acid in relation to structural materials, as a rule, increases with lowering of concentration. Thus, aluminum pertains to the category of "stable" materials with respect to 98-100% acid, and with dilution to 50-60% passes into the "unstable" group.

For decrease of corrosion into nitric acid there are introduced inhibitors – substances which lower corrosion. As inhibitor for nitric acid there is used for example, sulfuric acid.

As inhibitor there can be used orthophosphoric acid, which substantially lowers corrosion with content all of 1% in nitric acid.

A good inhibitor for nitric acid is hydrofluoric acid HF. Small addition of it (0.5-0.6%), while not practically lowering the calorific value, sharply lowers the corrosivity of nitric acid, especially in gaseous phase.

Industry produces concentrated nitric acid of two types; second type – 96-98% concentration, the first type – concentration not lower than 98%.

Nitric acid is a toxic product. Its vapors and nitrogen dioxide, always present in them, if inhaled may cause poisoning resulting in death.

Tetranitromethane $C(NO_2)_4$. Tetranitromethane is tetrasubstituted nitromethane with a high content of active oxygen (65.3%). This heavy, mobile, transparent liquid is of greenish-yellow color with sharp specific odor. Tetranitromethane is not hygroscopic. Water solubility in it at room temperature is 0.02%.

When working with tetranitromethane one should observe great accuracy, while not allowing organic substances to get in it.

An obstacle to the wide application of tetranitromethane in rocket technology is its high freezing point +13.8°C and danger of explosion.

Tetranitromethane is a highly toxic product. In toxicity it can be equated to nitrogen tetroxide.

Nitrogen tetroxide N_2O_4. Nitrogen tetroxide is a condensation product of nitrogen dioxide – substances widely used as an intermediate product in producing nitric acid by the synthetic method.

Nitrogen tetroxide is a light-yellow, highly volatile, highly mobile, heavy liquid. With increase of temperature from (-10.0°C) to (+21.0°C) the color of the liquid changes from light-yellow to reddish brown, which is connected with dissociation of N_2O_4 by NO_2, having a brown color.

In Figures V.15-V.18 there are given temperature dependences of certain physicochemical characteristics of nitrogen tetroxide. It dissolves (without interaction) many organic compounds (paraffin, naphthenic, aromatic hydrocarbons and their nitro derivatives) well. Unsaturated hydrocarbons, terpenes and amines react violently with N_2O_4. Reactions occur with strong increase of temperature and are often finished by ignition.

Nitrogen tetroxide with water content less than 0.1% is a substance that is corrosion passive, and can be stored and transported in tanks and drums of usual (unalloyed) steels. With increase of water content the corrosivity of nitrogen tetroxide sharply increases. During storage of nitrogen tetroxide it is necessary to provide complete hermetic sealing of tanks, since due to the high volatility and hygroscopicity the humid vapors of N_2O_4 can cause intense corrosion

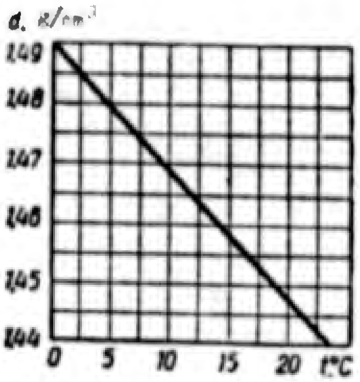

Fig. V.15.

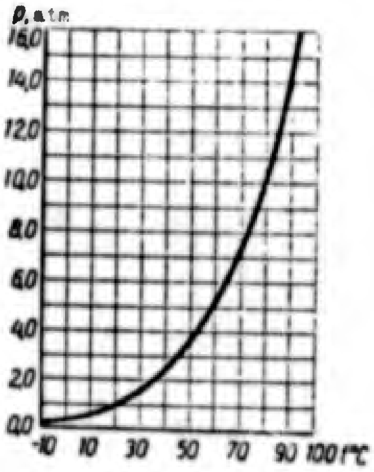

Fig. V.16.

Fig. V.15. Dependence of specific gravity of nitrogen tetroxide on temperature.

Fig. V.16. Dependence of vapor tension of nitrogen tetroxide on temperature.

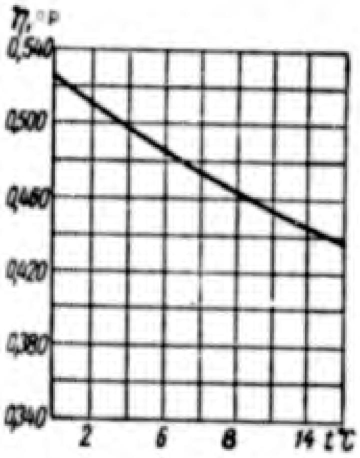

Fig. V.17.

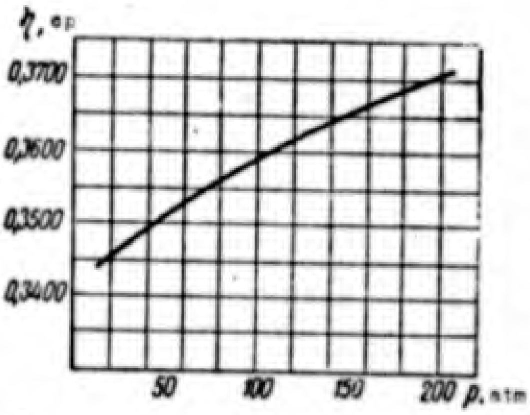

Fig. V.18.

Fig. V.17. Dependence of viscosity of nitrogen tetroxide on temperature.

Fig. V.18. Dependence of viscosity of nitrogen tetroxide on pressure at a temperature higher than the boiling point (t = 37.8°C).

of the external surfaces of tanks and surrounding objects.

Nitrogen tetroxide possesses high toxicity (is blood poison).

The basic operational deficiency of nitrogen tetroxide is its high freezing point (-11.23°C). This deficiency can be removed by introduction to nitrogen tetroxide of substances which lower the freezing temperature of oxidizer without an essential lowering of its energy characteristics. Nitrogen oxide NO can be used as such a substance. Freezing point of N_2O_4 + NO mixtures depending on NO content is shown in Fig. V.19.

Introduction of NO into N_2O_4 does not practically impair the energy characteristics and corrosion properties of oxidizer. However, vapor tension essentially increases simultaneously with lowering of freezing point and the boiling point of oxidizer is reduced. Figure V.20 shows change of vapor tension of NO + N_2O_4 system depending on temperature and percentage of NO.

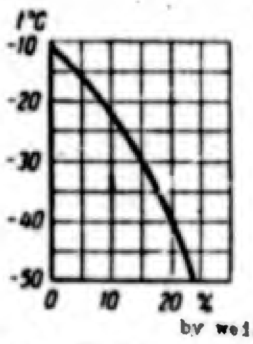

Fig. V.19.

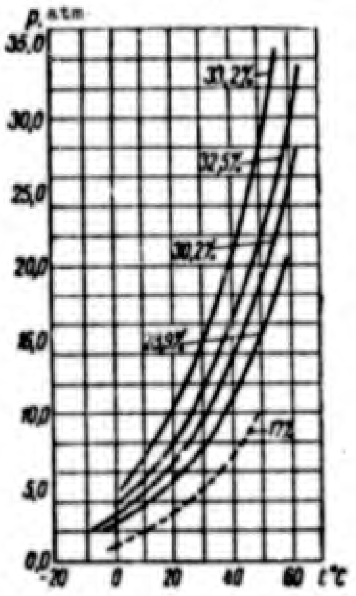

Fig. V.20.

Fig. V.19. Dependence of freezing point of NO - NO_2 system on NC content.

Fig. V.20. Dependence of vapor tension of NO - N_2O_4 system on temperature and content of NO in % by weight.

Introduction of nitrogen oxide into nitrogen tetroxide somewhat lowers the specific gravity of oxidizer.

As was already indicated, concentrated nitric acid is a thermally unstable substance, that makes its application as rocket propellant oxidizer impossible in objects requiring prolonged storage in equipped state. Thermal decomposition of nitric acid is a reversible process

$$2HNO_3 \rightleftharpoons 2NO_2 + 0.5O_2 + H_2O.$$

As in any reversible chemical reaction, equilibrium can be displaced to the left by introduction of excess of some products of reaction. Consequently, in order to suppress the decomposition of nitric acid, in our case it is necessary to introduce an excess of either NO_2 or H_2O. For rocket propellant oxidizer the introduction of water is inexpedient, since this will lead to lowering of the calorific value and specific thrust of propellant. Introduction of NO_2 (or N_2O_4), besides suppression of nitric acid decomposition, leads to increase of specific thrust of propellant, specific gravity, to lowering of freezing point and to increase of vapor tension of oxidizer.

In Figures V.21-V.25 there are shown dependences of specific gravity, vapor tension, boiling point, freezing point and heat capacity of nitrogen tetroxide solutions in nitric acid on concentration of N_2O_4, and in Fig. V.26 – dependence of viscosity of oxidizer with 14% N_2O_4 and 2% H_2O on temperature. Introduction of nitrogen tetroxide with specific gravity 1.45 g/cm^3 into nitric acid with specific gravity 1.504 g/cm^3 gives solutions with specific gravity essentially higher than pure nitric acid, for example 1.5838 g/cm^3 for 20% solution. Freezing point of oxidizer is lowered in proportion to increase of nitrogen tetroxide content up to 18%. A solution of such concentration has minimum freezing point (-73°C). Further increase of N_2O_4 content leads to increase of freezing point. Boiling point of solutions with more than 20% N_2O_4 content is already lower than 50°C, which naturally leads to complication of the treatment of such oxidizers.

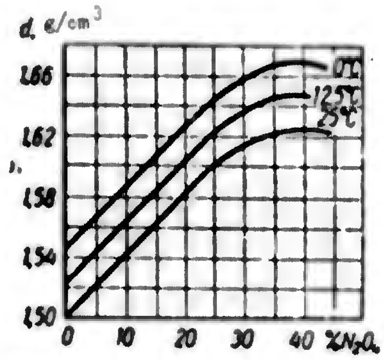

Fig. V.21.

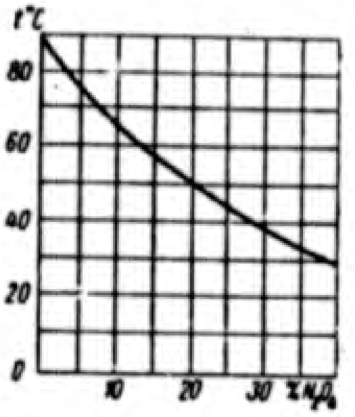

Fig. V.22.

Fig. V.21. Dependence of specific gravity of nitrogen tetroxide solutions in nitric acid on N_2O_4 content.

Fig. V.22. Dependence of boiling point of nitrogen tetroxide solutions in nitric acid on N_2O_4 content.

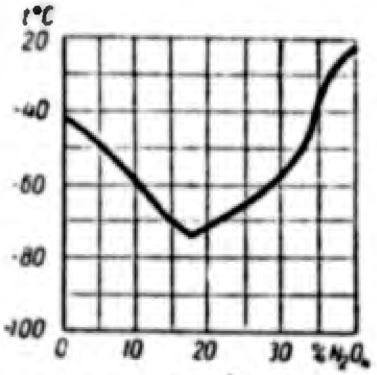

Fig. V.23.

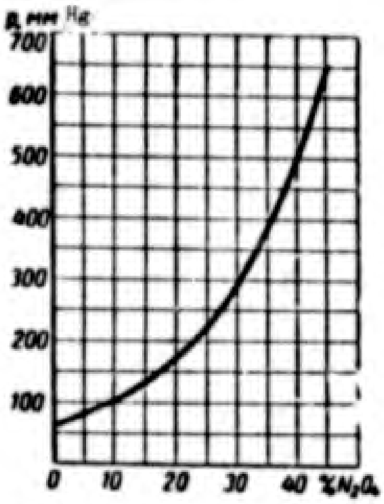

Fig. V.24.

Fig. V.23. Dependence of freezing point of nitrogen tetroxide solutions in nitric acid on N_2O_4 content.

Fig. V.24. Dependence of vapor tension of nitrogen tetroxide solutions in nitric acid on N_2O_4 content (at a temperature of +25°C).

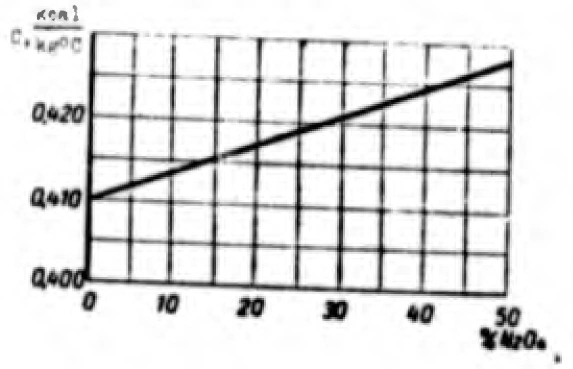

Fig. V.25. Dependence of heat of dissolution of nitrogen tetroxide in nitric acid on N_2O_4 content.

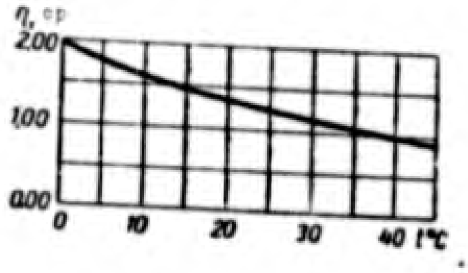

Fig. V.26. Dependence of viscosity of red-fumming nitric acid (composition: HNO_3 – 84.0%, N_2O_4 – 14.0%, H_2O – 2.0%) on temperature.

With respect to corrosivity the oxidizers of such type scarcely differ from nitric acid and require the same structural materials. Introduction of 0.5-0.6% hydrofluoric acid to this oxidizer lowers its corrosivity. Toxicity of N_2O_4 solutions in HNO_3 is higher than that of pure nitric acid.

Hydrogen peroxide H_2O_2. Hydrogen peroxide is an oxidizer, easy separating active free oxygen. High-concentration solutions of hydrogen peroxide (80% and higher) are of interest for rocket technology.

Basic physicochemical characteristics of 100% hydrogen peroxide are given in Table V.1.

The presence of water in hydrogen peroxide, with which it is mixed in any ratios, essentially changes the physicochemical characteristics, shown in Figs. V.27-V.32.

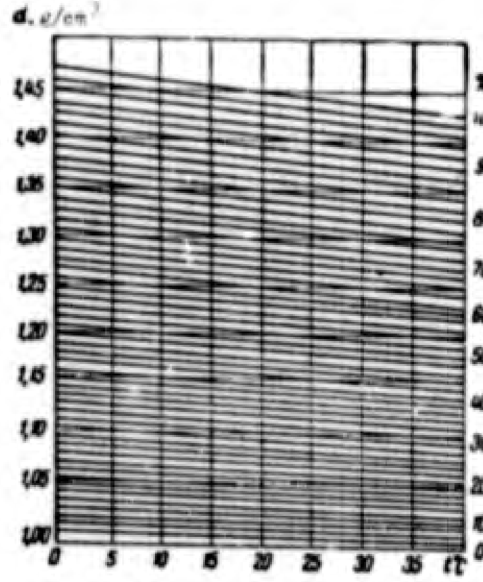

Fig. V.27. Dependence of specific gravity of aqueous solutions of hydrogen peroxide on concentration and temperature.

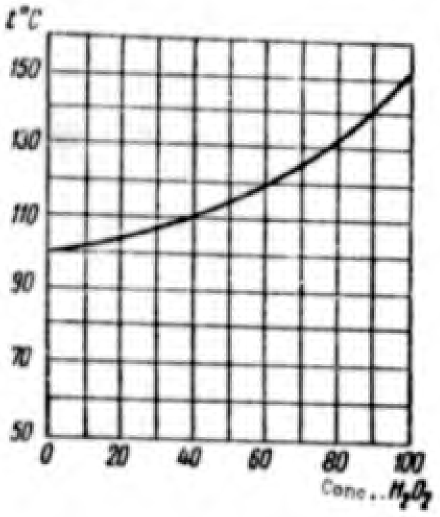

Fig. V.28. Dependence of boiling point of aqueous solutions of hydrogen peroxide on temperature.

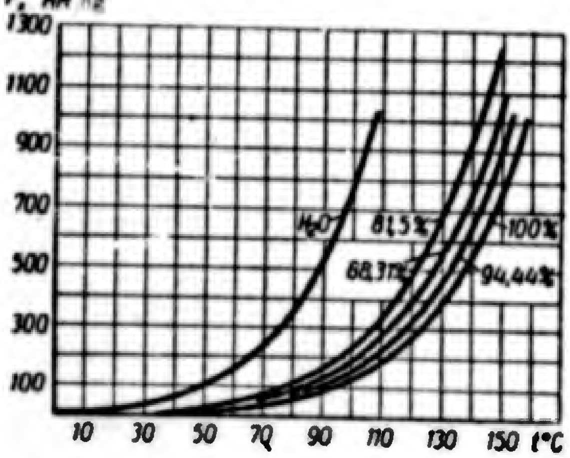

Fig. V.29. Dependence of vapor tension of aqueous solution of hydrogen peroxide on temperature and concentration.

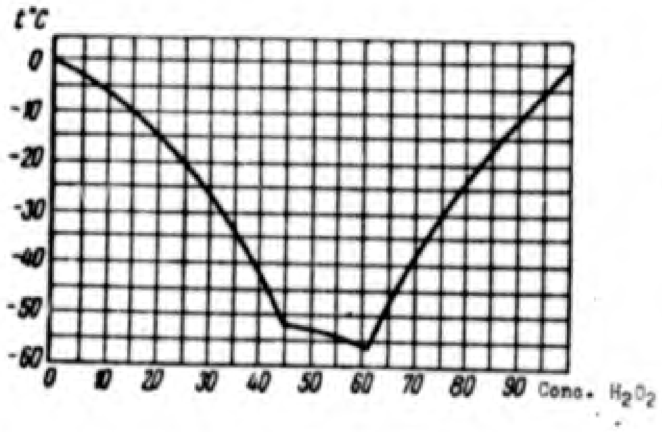

Fig. V.30. Dependence of freezing point of aqueous solutions of hydrogen peroxide on concentration.

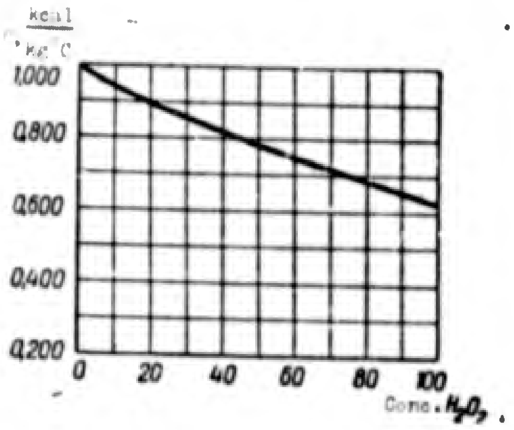

Fig. V.31. Dependence of heat capacity of hydrogen peroxide solutions on the concentration in temperature range 0-27°C.

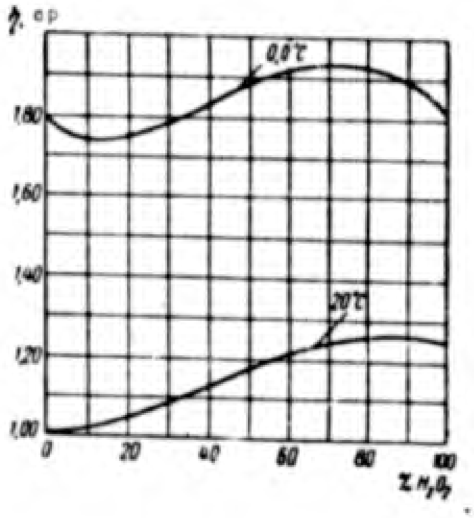

Fig. V.32. Dependence of viscosity of aqueous solutions of hydrogen peroxide on concentration and temperature.

Concentration hydrogen peroxide is a colorless, transparent heavy solution. It is easily decomposed under action of various (even in very small quantites) impurities

$$H_2O_2 \rightarrow H_2O + 0.5O_2.$$

Decomposition is accompanied by considerable heat liberation (12.975 kcal/mole or 381 kcal/kg). Rate of decomposition of hydrogen peroxide free from impurities is small and rises with increase of temperature. During contamination the decomposition of hydrogen peroxide can take a self-accelerating character and lead to an explosion. For preventing this we introduce stabilizers - phosphoric acid, mixture of sodium stannate with sodium pyrophosphate or a mixture of 8-hydroxyquinoline with sodium pyrophosphate. Substances which cause acceleration of hydrogen peroxide decomposition include oxides and salts of heavy metals (lead, manganese, mercury, silver, and iron); metals (silver, gold, platinum).

Mixtures of H_2O_2 with organic substances in a wide range of ratios are very sensitive to external pulses by explosives.

Structural and sealing materials for hydrogen peroxide are aluminum, chromium and chromium-nickel stainless steels, fluorinated or chlorinated polyethylene or polyvinyl plastics. The application of usual "ferrous" metals, copper, and lead is impermissible.

Storage and transportation of hydrogen peroxide is accomplished in pure aluminum tanks. Its brief storage in tanks made from chromium and chromium-nickel steels is permissible. Before filling with hydrogen peroxide the tanks must be subjected to special treatment by alkali and nitric acid.

Tanks with H_2O_2 must be connected with the atmosphere with the aid of drain pipes, and equipped with filters, excluding the possibility of dust entering from the air.

Hydrogen peroxide is a toxic product. High concentration of H_2O_2 vapors in air causes irritation of the mucous membranes of the eyes and nasopharynx.

Chlorine trifluoride ClF_3. Chlorine trifluoride belongs to halide compounds of fluorine. Temperature dependences of specific gravity and vapor tension of chlorine trifluoride are shown in Figs. V.33 and V.34.

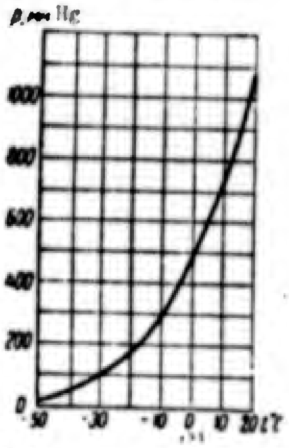

Fig. V.33.

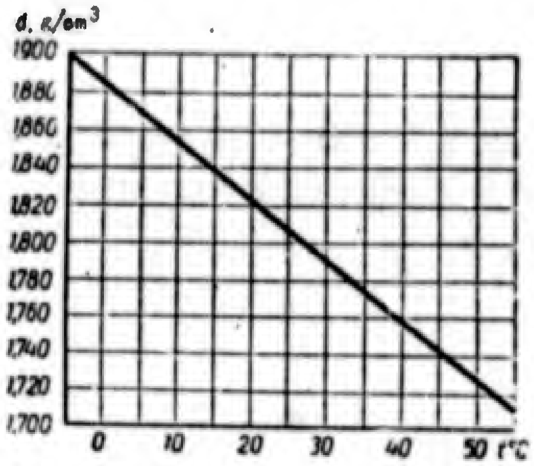

Fig. V.34.

Fig. V.33. Dependence of vapor tension of chlorine trifluoride on temperature.

Fig. V.34. Dependence of specific gravity of chlorine trifluoride on temperature.

Chlorine trifluoride is a slightly greenish, heavy, mobile liquid. Chlorine trifluoride is a very active oxidizer. Many organic substances ignite upon contact with it. Interaction of ClF_3 with water occurs with an explosion.

Chlorine trifluoride actively interacts with most metals with the formation of a protective film of fluoride, preventing its further destruction. For the manufacture of tanks for chlorine trifluoride, brass, copper, magnesium alloys, standard mild steels and nickel are suitable. Storage and transportation of chlorine trifluoride must be accomplished under conditions of complete airtightness under pressure of its own vapors (at +50°C – 5 atm).

Toxicity of chlorine trifluoride is equated to that of elementary fluorine.

<u>Perchloryl fluoride</u> $FClO_3$. Perchloryl fluoride is a colorless liquid. It is not sensitive to impact and other initiators of explosion, however it will form explosive mixtures with combustible substances. With certain organic substances it reacts with self-ignition. Waterless perchloryl fluoride is corrosion passive and can be stored in glass and metal containers. In the presence of moisture

it causes corrosion of the majority of metals.

Toxicity of perchloryl fluoride is essentially lower than that of other fluorine-containing oxidizers.

§ 4. Rocket Propellant Fuels

Since the energy properties of fuels, determining the efficiency of rocket propellants (calorific value, specific gas constant of combustion products and ratio of heat capacities of combustion products), are additive properties, then in the first approximation[1] the efficiency of fuel will be determined by ratios and energy properties of the elements entering the composition of fuel. The greatest calorific value is possessed by elements of the first three periods of D. I. Mendeleyev's table (H, Li, Be, B, C, Mg, Al, Si, etc). Most of these elements during combustion with oxygen give oxides with high boiling temperatures (Li_2O – $t_{\text{кип}} = 2600^\circ C$, BeO – $t_{\text{кип}} \approx 4100^\circ C$; MgO – $t_{\text{субл}} = 2800^\circ C$; Al_2O_3 – $t_{\text{кип}} = 2890^\circ C$; SiO_2 – $t_{\text{кип}} = 2590^\circ C$). The presence in combustion products of substances in condensed (liquid or solid) state will lower the exit velocity, and consequently the specific thrust of propellant. If we assume that these oxides will be in the combustion chamber in gaseous state, then (due to very high values of heats of evaporation) the calorific value of these elements (lowest calorific value) becomes essentially lower than that of carbon, and in the case of beryllium the heats of combustion reaction will not even suffice for complete evaporation of the forming oxide. Therefore, the application of such elements as Li, Be, Mg, Al, and Si as compound elements of combustibles for rocket propellants based on oxygen-containing oxidizers is impossible to recognize as expedient. Boron, forming oxide B_2O_3 with $t_{\text{кип}} = 1680^\circ C$ and relatively low heat of evaporation, occupies a somewhat special position. The lowest calorific value of boron with oxygen (2973 kcal/kg) is somewhat lower than the calorific value of hydrogen (3210 kcal/kg), but is substantially higher than that of carbon (2137 kcal/kg) and hydrocarbons of type C_nH_{2n+2} (2400 kcal/kg). However, the low value of gas formation (322 l/kg) and low value of c_p/c_v for pentatomic molecule B_2O_3 sharply lowers the efficiency of boron as fuel for rocket propellants.

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[1] Energy characteristics of fuels are definitely affected by heat of formation of fuel molecule; but due to the fact that the quantity of combustible in propellant is only 15-25% (by weight), this effect is small and according to preliminary evaluation cannot be considered.

According to calculated data the use of boron hydrides (diborane B_2H_6 and pentaborane B_5H_9) with hydrogen peroxide can be of some interest.

During the use of oxygen-containing oxidizers the application of hydrogen and hydrocarbons with maximum hydrogen content as fuels is expedient.

During combustion the examined elements with fluorine will form fluorides, having considerably lower (in comparsion with oxides) boiling points (LiF – $t_{кип}$ = 1681°C; BF_3 – $t_{кип}$ = -101°C; MgF_2 – $t_{кип}$ = 2277°C; AlF_3 – $t_{кип}$ = 2160°C; SiF_4 – $t_{кип}$ = -65°C), and also lower values of heats of evaporation.

However, polyatomic molecules with high molecular weights, of the majority of fluorides (as in the case of oxides) give combustion products with low values of gas formation and ratio of heat capacities c_p/c_v, which makes the application of such elements as silicon, aluminum, magnesium, carbon and boron with fluorine-containing oxidizers show little promise. For fluorine-containing oxidizers fuels containing hydrogen, and possibly lithium and beryllium are of interest.

The presence of nitrogen in the fuel lowers the calorific value of propellant based on both oxygen-containing and fluorine-containing oxidizers; however the presence of diatomic molecule N_2 with relatively small molecular weight in combustion products can improve the characteristics of the working medium and in some cases can even increase the specific thrust of the propellant.

The presence of oxidizing elements (oxygen, fluorine, chlorine) in fuel, as a rule, lowers the effectiveness of the propellant.

Alcohols, hydrocarbons, amines, hydrazine and its derivatives, hydrogen, ammonia and so forth received the lowest practical application in rocket technology. Basic physicochemical characteristics of these fuels are given in Table V.2.

Table V.2.

Designation of fuel	Chemical formula	Molecular weight	Boiling point, °C	Freezing point, °C	Specific gravity of liquid, g/cm³	Critical temperature, °C	Critical pressure, atm	Heat of fusion, kcal/kg	Heat of evaporation, kcal/kg
Hydrogen....................	H_2	2,016	−252,8	−259,2	0,0709 (−253°C)	−239,9	12,8	13,8	108,0
Ammonia.....................	NH_3	17,032	−33,36	−77,75	0,6814 (−77,7°C) 0,6080 (22,2°C)	132,4	111,5	83,9	327,08
Aliphatic amines									
Diethylamine................	$(C_2H_5)_2NH$	73,14	56,2	−50,0	0,7056 (20°C)	223,3	36,58	−	90,2
Triethylamine...............	$(C_2H_5)_3N$	101,19	89,5	[illegible]	0,729 (20°C)	−	−	−	74,35
Ethylenediamine.............	$(NH_2)_2C_2H_4$	60,10	116,1	+8,5	0,8994 (20°C)	−	−	77,0	167,0
Diethylenetriamine..........	$(NH_2C_2H_4)_2NH$	103,17	206,7	−39,0	0,956 (20°C)	−	−	−	119,2
Aromatic amines									
Aniline.....................	$C_6H_5NH_2$	93,12	184,4	−6,15	1,022 (20°C)	−	−	37,0	104,27
Toluidine...................	$CH_3C_6H_4NH_2$	107,16	200,2	−24,4	0,998 (20°C)	−	−	−	95,10
m-xylidine..................	$(CH_3)_2C_6H_3NH_2$	121,18	212,0	−	0,9783 (20°C)	−	−	−	90,34
Hydrazine derivatives									
Hydrazine...................	N_2H_4	32,05	113,5	+2,0	1,0085 (20°C)	380,0	145,0	94,5	333,85
Monomethylhydrazine.........	$CH_3NH{-}NH_2$	46,075	87,5	−52,4	0,874 (25°C)	−	−	−	−
Dimethylhydrazine...........	$(CH_3)_2{-}N_2H_2$	60,078	63,0	−57,0	0,7914 (22°C)	249,0	60,0	40,0	139,3
Kerosene....................	$C_{10}H_{20}$	140	−	−43	0,8 (25°C)	−	−	−	−

Table V.2 (Continued).

Designation of fuel	Heat capacity, kcal/kg°C	Coefficient of thermal conductivity, kcal/m·h°C	Heat of formation, kcal/kg	Viscosity, cp	Surface tension, dyn/cm	Vapor tension at +50°C*, atm
Hydrogen	2,294 (−253°C)	–	0,000 (gas)	$0{,}1300\cdot10^{-2}$ (−253°C)	2,35 (−253°C)	–
Ammonia	1,062 (−70,6°C) 1,068 (−31,7°C)	0,043 (0,–C)	−930,12 (gas) −640,13 (liquid)	0,246 (−33,5°C)	34,30 (−34°C)	20,0
Aliphatic amines						
Diethylamine	0,516 (20°C)		−3[illegible],80 (liquid)		18,2 (2[illegible]°C)	–
Triethylamine	0,45 (20°C)	0,104 (20°C)	−3[illegible],33 (liquid)	0,363 (25°C)	20,66 (20°C)	0,36
Ethylenediamine	–	–	−165,8 (liquid)	1,54 (25°C)	–	0,013 (21°C)
Diethylenetriamine	–	–		8,3 (15°C)	–	0,006 (100°C)
Aromatic amines						
Aniline	0,521 (20°C)	0,1535 (17°C)	80,635 (liquid)	4,40 (20°C)	44,1 (10°C)	0,006
Toluidine	–	–	−61,34 (liquid)	4,35 (20°C)	40,0 (20°C)	0,002
m-xylidine	–	0,180 (21°C)	−125,4 (liquid)	4,9 (15°C)	36,6 (20°C)	0,379 (170°C)
Hydrazine derivatives						
Hydrazine	0,737 (25°C)	0,18 (20°C)	378,80 (liquid)	0,974 (20°C)	74,76 (20°C)	0,06
Monomethylhydrazine	–	–	275,67 (liquid)	–	–	0,225
Dimethylhydrazine	0,653 (25°C)	0,1706 (25°C)	187,3 (liquid)	0,556 (15,6°C)	28,0 (20°C)	0,75
Kerosene	0.5	0,134 (0°C)	−421,5 (liquid)	1,6 (15°C)	–	0,01 (40°C)

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*In cases when vapor tensions are given for temperatures which are different from +50°C, in parentheses there are shown temperatures to which the given values of vapor tension correspond.

Hydrogen (H_2). Hydrogen is one of the promising fuels.

Gaseous hydrogen is a light gas without color, odor and taste, easily penetrating even glass, quartz and certain metals at elevated temperature.

Liquid hydrogen is a transparent, colorless, mobile liquid.

Molecular hydrogen exists in two forms: ortho- and parahydrogen. Equilibrium ratios between these forms depend on temperature. Transition of orthohydrogen into parahydrogen (ortho- para-conversion) is accompanied by considerable heat liberation (168.14 kcal/kg at -253°C), sufficient for evaporation of all liquid hydrogen. At present there are found effective catalysts, allowing accomplishment of ortho- and para-conversion until liquefaction of hydrogen and by this considerably lowering losses of liquid hydrogen during storage.

In pure form hydrogen is a nondangerously explosive substance. However, mixtures of it with oxygen and air in a wide range of ratios are able to explode from the action of thermal or electrical pulse. Concentration limits of explosibility for hydrogen-air mixtures are 9.5 and 65.2% hydrogen in the mixture, for hydrogen-oxygen mixtures 9.2 and 91.6% hydrogen in the mixture.

Thanks to the very low critical temperature of hydrogen, it is possible to store it in liquid form only under the condition of venting of tanks. For exclusion of the possibility of atmospheric air getting in liquid hydrogen the vents must be equipped with hydraulic seals. The evaporating hydrogen should be trapped, and the location well ventilated. Hydrogen is not toxic, but inhalation of large quantities of hydrogen can lead to suffocation.

Ammonia NH_3. Ammonia is produced in industry mainly by direct synthesis from nitrogen and hydrogen on catalysts. Dependence of vapor tension of ammonia on temperature is shown on Fig. V.35. Liquid ammonia is a colorless mobile liquid.

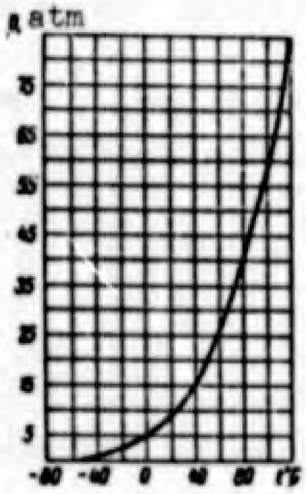

Fig. V.35. Dependence of vapor tension of ammonia on temperature.

Ammonia is a chemically stable compound, not decomposing while heating to 350°C. Liquid ammonia dissolves hydrogen well, and also alkali-earth metals, with which it will form amides. With air and oxygen it will form explosive mixtures within limits of ammonia content 14.5-26.8% and 13.5-82.0% in air and oxygen respectively.

High value of critical temperature permits storing and transporting liquid ammonia under low pressure (vapor tension of ammonia at +50°C is ~20 atm).

Ammonia is toxic, and with prolonged inhaling may cause poisoning, resulting in death.

Amines. Amines are organic derivatives of ammonia, for which one, two, or three atoms of hydrogen are replaced by organic radicals.[1]

Of the aliphatic amines diethylamine $(C_2H_5)_2NH$, triethylamine $(C_2H_5)_3N$, ethylenediamine $NH_2CH_2CH_2NH_2$ and diethylenetriamine $NH_2C_2H_4NHC_2H_4NH_2$ are of interest for rocket technology. Aliphatic amines are mobile, transparent, colorless or slightly yellowish

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[1] Amines, in which the replacing radicals are hydrocarbons with open chain of carbon atoms (methyl – CH_3; ethyl – C_2H_5 and others), are called aliphatic or "fatty" amines. If the replacing radicals contain benzene rings of carbon atoms, then such amines are called aromatic.

liquids, and well soluble in water.

Aromatic amines include aniline $C_6H_5NH_2$, toluidines $CH_3C_5H_4NH_2$ and xylidines $(CH_3)_2C_6H_3NH_2$.

Aromatic amines are colored (most often reddish-brown) liquids, poorly soluble in water, and mixed well with alcohols and aliphatic amines. A characteristic property for all amines is violent interaction with concentrated nitric acid and nitrogen tetroxide, leading, as a rule, to self-ignition with a small period of induction[1] (self-ignition delay) — 0.3-0.4 s. Corrosivity of amines is low. Amines are stored and transported in large tanks made from usual "ferrous" metals.

Amines are highly toxic products.

For improvement of physicochemical and starting characteristics of propellants there are used blends of two and more components. For example, blends (50/50) of triethylamine and xylidine, blends of 20% aniline and 80% furfuryl alcohol and others received practical application.

Hydrazine N_2H_4. Hydrazine is a derivative of ammonia. Dependence of vapor tension of hydrazine on temperature is shown in Fig. V.36.

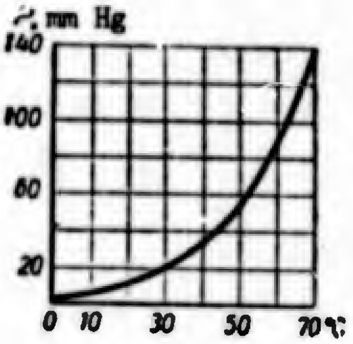

Fig. V.36. Dependence of vapor tension of hydrazine on temperature.

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[1] Period of induction or self-ignition delay is the time from the moment the combustible contacts the oxidizer until the appearance of flame.

Hydrazine is a colorless, transparent, hygroscopic liquid with a characteristic ammonium odor. Hydrazine is thermodynamically unstable, and is easily decomposed under the influence of different catalysts (oxides of certain metals, carbon, asbestos) or heating. While heating to 230°C there occurs explosive decomposition of hydrazine. Flash point of hydrazine in air is 38°C. Waterless hydrazine self-ignites with halides, liquid oxygen, hydrogen peroxide and other strong oxidizers. Mixtures of hydrazine vapors with air ignite over a wide range from 4.6% to 100% (by volume) hydrazine in the mixture. Hydrazine is mixed well with water, alcohols, ammonia and amines. It is not dissolved in hydrocarbons. Hydrazine will form eutectic mixture (13% hydrazine in mixture) with ammonia with melting point -80°C. Lowering of melting point is also attained by dissolution in hydrazine of lithium borhydride $LiBH_4$, prussic acid HCN, ammonium thiocyanate NH_4SCN, and also derivatives of hydrazine — monomethylhydrazine and dimethylhydrazine. Mixture of hydrazine with dimethylhydrazine (50/50) is used as fuel of rocket propellants.

Hydrazine is corrosionally active. Aluminum, its alloys, and stainless steels are stable in hydrazine. As packing material it is possible to use polyethylene.

Hydrazine is toxic, is irritating to mucous membrane of the eyes, and may cause temporary blindness.

Asymmetrical dimethylhydrazine $[(CH_3)_2N\text{-}NH_2]$. Dimethylhydrazine is a derivative of hydrazine, in which two atoms of hydrogen are replaced by methyl radicals CH_3.

In contrast to symmetrical dimethylhydrazine $[(CH_3)HN\text{-}NH(CH_3)]$, in asymmetrical dimethylhydrazine both methyl radicals are connected with one atom of nitrogen.

Asymmetric dimethylhydrazine is a colorless, transparent, hygroscopic liquid.

Asymmetric dimethylhydrazine is a thermally stable product. At usual temperature it interacts very slowly with air. Mixtures of its vapors with air are explodable in a wide range of ratios (from 2 to 99% dimizine by volume). Self-ignition temperature of dimethylhydrazine is 249°C.

Asymmetric dimethylhydrazine is very toxic, causes injury of the lungs and liver, and destroys red blood corpuscles.

Alcohols. Alcohols are derivatives of hydrocarbons and are characterized by the presence of hydroxyl group OH. Methyl, ethyl, and isopropyl alcohols received application in rocket technology. At present alcohols are almost completely displaced from rocket technology by more effective fuels (hydrocarbons, amines, hydrazine and its derivatives).

Fuels based on petroleum products. Petroleum is the most powerful natural source of hydrocarbon fuels. As rocket propellant there are mainly used kerosene fractions of petroleum, i.e., fractions with boiling point up to 250-300°C. For improvement of physico-chemical, energy and cooling properties the kerosene fractions are subjected to various treatment (purification from sulfurous compounds, removal of aromatic hydrocarbons, increase of content of naphthenic hydrocarbons and others).

In Table V.3 there are given basic characteristics of fuels based on petroleum refining products. These combustibles due to accessibility, inexpensiveness, supply of raw material and industrial base can be widely used in rocket propellants on an oxygen base. Fuels based on petroleum products are corrosionally passive, are not toxic, and are safe in handling with observance of standard rules of handling combustible materials.

Table V.3.

Composition, % (by weight)		Specific gravity (20°C), g/cm³	Temperature of start of boiling, °C	Freezing point, °C	Viscosity, cSt	Heat of combustion (lowest), kcal/kg
hydrogen	carbon					
13,38—13,68	86,02—86,04	0,809—0,823	122—141	—60	1,70—191 (20°C) 2,67—2,94 (0°C) 5,0 —16,3 (—40°C)	10250—10315
14,05	85,75	0,773—0,789	122—140	—60	1,15—1,59 (20°C) 1,78—1,94 (0°C) 4,63—5,06 (—40°C)	10350—10390
14,22—14,34	85,6 —85,72	0,758—0,770	58—74	—57	1,05—1,40 (20°C) 1,40—1,57 (0°C) 3,12—3,98 (—40°C)	10290—10380
14,09—14,33	85,34—85,88	0,769—0,784	78—95	—55	1,06—1,28 (20°C) 1,26—1,84 (0°C) 3,06—4,39 (—40°C)	10275—10370

§ 5. Separately Fed Propellants

In view of the fact that oxidizers make up the principal part of propellant and their list is limited by a small quantity of substances, it is accepted to group separately fed propellants and to name them by oxidizers (propellant on oxygen base, propellant on nitric acid base, etc.). In Tables V.4 and V.5 there are given energy characteristics of certain liquid rocket propellants with expansion ratio $\frac{p_k}{p_c} = 70$ and equilibrium outflow.

Propellants Based on Low-Boiling Oxidizers

Propellants on oxygen and ozone base. Application of propellants on liquid oxygen base (combined with liquid hydrogen or liquid hydrocarbons) was recommended in 1903 by K. E. Tsiolkovskiy.

The proposal to use ozone as rocket propellant oxidizer also belongs to K. E. Tsiolkovskiy. Analysis of data of Table V.4 shows that propellants on ozone base will permit obtaining considerably higher specific thrusts and higher specific gravity of propellants than in case of propellants on oxygen base. Solutions of ozone in oxygen give propellants with intermediate values of specific thrust.

However, the very high tendency of ozone and its solutions in oxygen (concentration more than 20%) to explosive decomposition under action of various external influences complicates the use of propellants based on ozone or its solutions in oxygen for liquid-propellant rocket engines.

Propellants on fluorine base. The assumption of expediency of application of fluuorine as rocket propellant oxidizer was expressed for the first time in 1932 by F. A. Tsander. Advantages of propellants based on fluorine (as compared to propellants on oxygen base) are higher specific thrusts and higher specific gravities. At the same time, propellants on fluorine base are dangerous in handling and require satisfaction of a number of additional safety engineering conditions during operation of similar liquid-propellant rocket

Table V.4.

Propellant		T °K	$R_{уд}$ $\frac{kg \cdot s}{kg}$
oxidizer	fuel		
Liquid oxygen O_2	Hydrogen H_2	2997	391
	Pentaborane B_5H_9	4518	327
	Methylhydrazine $N_2H_3CH_3$	3144	313
	Dimethylhydrazine asymmetric $N_2H_2(CH_3)_2$	3594	310
	Kerosene	3695	298
	Ammonia NH_3	3039	294
Liquid Fluorine F_2	Hydrogen H_2	3869	410
	Lithium Li	5500	382
	Hydrazine N_2H_4	4675	363
	Pentaborane B_5H_9	5101	360
	Ammonia NH_3	4542	357
	Dimethylhydrazine asymmetric $N_2H_2(CH_3)_2$	—	344
Fluorine dioxide F_2	Pentaborane B_5H_9	5169	367
	Ammonia NH_3	3613	260
	Hydrazine N_2H_4	3525	257
Nitrogen trifluoride	Pentaborane B_5H_9	—	326
	Hydrazine N_2H_4	4105	305
Fluorine chlorate $FClO_3$	Hydrogen H_2	2744	344
	Pentaborane B_5H_9	4447	306
	Hydrazine N_2H_4	3466	295
	Dimethylhydrazine asymmetric $N_2H_2(CH_3)_2$	3666	290

Table V.4 (Continued).

Propellant		T °K	$R_{\text{уд}}$ $\frac{kg \cdot s}{kg}$
oxidizer	fuel		
Ozone O_3	Hydrogen H_2	2944	–
	Ammonia NH_3	3350	315
Nitrogen tetrafluoride	Hydrazine N_2H_4	4431	332

Table V.5.

Propellant		T °K	$R_{\text{уд}}$ $\frac{kg \cdot s}{kg}$
oxidizer	fuel		
Nitrogen tetroxide	Pentaborane B_5H_9	4266	296
	Hydrazine N_2H_4	2994	292
	Methylhydrazine $N_2H_3CH_3$	3361	288
	Hydrazine (50%) + asymmetric dimethylhydrazine (50%)	3363	288
	Dimethylhydrazine asymmetric $N_2H_2(CH_3)_2$	3192	285
	Kerosene	3335	270
Nitric acid HNO_3 (78%) + nitrogen tetroxide N_2O_4	Hydrazine N_2H_4	2828	283
	Methylhydrazine $N_2H_3CH_3$	3172	279
	Dimethylhydrazine asymmetric $N_2H_2(CH_3)_2$	–	272

Table V.5 (Continued).

Propellant		T °K	$R_{уд}$ $\frac{kg\cdot s}{kg}$
oxidizer	fuel		
Nitrogen tetroxide N_2O_4 (85%) + nitrogen oxide NO (15%)	Pentaborane B_5H_9	—	302
	Methylhydrazine $N_2H_3CH_3$	—	290
	Dimethylhydrazine asymmetric $N_2H_2(CH_3)_2$	—	288
Hydrogen peroxide (95%) H_2O_2	Pentaborane B_5H_9	3400	312
	Hydrazine N_2H_4	2597	282
	Methylhydrazine $N_2H_3CH_3$	2900	279
	Kerosene	2914	273
Chlorine trifluoride ClF_3	Lithium Li	5200	332
	Hydrazine N_2H_4	3896	292
	Pentaborane B_5H_9	4487	288
	Methylhydrazine $N_2H_3CH_3$	3803	283
	Dimethylhydrazine asymmetric $N_2H_2(CH_3)_2$	3383	280

engines. Therefore, the application of only those propellants which will permit obtaining specific thrusts, which are unattainable with application of propellants on oxygen base, will be expedient. Such fuels are hydrogen + fluorine, hydrazine + fluorine and ammonia + + fluorine, i.e., propellants with the use of fuels not containing carbon. The presence of carbon in fuel leads to the formation of pentatomic molecule CF_4, the presence of which in combustion products sharply lowers the exit velocity and specific thrust. Ignition of propellants on fluorine base will not cause any difficulties, since the high chemical activity of fluorine ensures self-ignition upon contact with the majority of combustible substances. Works on the creation of new oxidizers on the basis of nitrogen trifluoride and tetrafluorohydrazine are of interest. These oxidizers are somewhat inferior to fluorine in energy characteristics, but possess the best operating characteristics (less toxicity, higher boiling point, less corrosivity).

Propellants on fluorine monoxide base. In case of carbonless fuels (hydrazine, ammonia), propellants on fluorine monoxide base give specific thrust, with average value between propellants on fluorine and oxygen base. In combination with hydrocarbons, amines and organic derivatives of hydrazine fluorine monoxide gives propellants, which substantially exceed both propellants on oxygen base and propellants on fluorine base (with the same fuels) in specific thrust.

Propellants on the Basis of High-Boiling Oxidizers

Propellants on nitric acid base. Nitric acid was proposed and experimentally tested as oxidizer of rocket propellants for the first time by V. P. Glushko in 1932.

As was already indicated, due to negative qualities (thermal instability, high corrosivity and others) nitric acid lost its value as rocket propellant oxidizer.

At present the most widely applied propellants are those on nitric acid base with the addition of nitrogen tetroxide with use of fuels: mixture of amines and dimethylhydrazine. Sometimes there are used hydrocarbon fuels. There are conducted wide investigations with monomethylhydrazine, certain new amines and mixtures of monomethylhydrazine and dimethylhydrazine with hydrazine and some di- and triamines. Fuels on the basis of amines and hydrazine derivatives self-ignite upon contact with oxidizers on the basis of nitric acid and nitrogen tetroxide and do not require any special means of ignition.

Propellants on nitrogen tetroxide base. Priority in the application of nitrogen tetroxide as rocket propellant oxidizer belongs to

V. P. Glushko, who in 1932 began experimental investigations with this oxidizer.

Propellants on nitrogen tetroxide base have 2-5% higher specific thrusts and 6-8% less specific gravity than propellants based on nitric acid.

Application of this oxidizer under winter conditions causes many difficulties due to its high freezing point (-11°C). In spite of the shown disadvantage, nitrogen tetroxide is widely used in rocket engine manufacture.

Propellants on tetranitromethane base. Propellants on tetranitromethane base in practice are not inferior to propellants on nitrogen tetroxide base with regard to specific thrust and considerably (by 8-12%) exceed them in specific gravity.

Due to the great danger of explosion, propellants on tetranitromethane base are rarely used.

Propellants on hydrogen peroxide base. Possibilities of hydrogen peroxide as rocket propellant oxidizer were analyzed by V. P. Glushko in USSR and German scientist E. Zenger in 1935.

Propellants on hydrogen peroxide base (concentration 95%) have more specific thrust than propellants on nitric acid base (with the same fuels). Specific gravities of propellants on hydrogen peroxide base are 3-7% higher than for propellants on nitrogen tetroxide base. High freezing point of concentrated hydrogen peroxide (-6°C for 95% concentration) and its slow decomposition during storage do not permit using propellants on its base for storable objects. For objects which are loaded before starting (especially for aviation objects), these propellants are of interest.

Propellants on chlorine trifluoride and perchloryl fluoride base. At present propellants on chlorine trifluoride base are considered as storable propellants. These propellants (in case of application as fuels of carbon-containing substances) give lower specific thrust than propellants on nitrogen tetroxide base. Lowering of specific thrust is greater, the higher the carbon content in fuel. Specific gravity of propellants on chlorine trifluoride base is substantially higher (by 14-22%) than for propellants on nitrogen tetroxide base.

High toxicity and high corrosivity complicate the use of this oxidizer, and its high cost and relatively low energy characteristics make its application scarcely expedient for mass objects.

Propellants on perchloryl fluoride base provide higher specific thrusts as compared to all the other propellants on the basis of high-boiling oxidizers. Operating characteristics of this oxidizer are as yet insufficiently studied.

§ 6. Monopropellants

At present monopropellants have been applied in rocket technology only as auxiliary energy sources for driving turbopump units, for flight stabilization systems, as airborne energy sources and others.

Theoretical calculations show that a number of individual substances (hydrazoic acid, acetylene, nitromethane, methyl nitrate and others) and various blends of combustibles with oxidizers can provide sufficiently high specific thrusts (in the limit the same as separately fed propellants). However, practice showed that creation of sufficient effective monopropellant turned out to be impossible due to the very high sensitivity of such propellants to explosion. Suppression of explosive properties is possible only by introduction of large quantities of ballasting additives, which sharply lower propellant efficiency. Energy characteristics of safety monopropellants are so low that it is inexpedient to apply them as basic propellants of liquid-propellant rocket engines. In Table V.6 there are given energy data of some monopropellants.

Concentrated hydrogen peroxide was the most widely applied as auxiliary energy source. In postwar years hydrogen peroxide

Table V.6.

Composition of propellant	Chemical formula	Pressure in combustion chamber, atm	Temperature in combustion chamber, °K	Specific gravity of propellant, g/cm³	Specific thrust, kg/kg/s
Hydrogen peroxide, 100%...........	H_2O_2	21,0	1253	1,463	146
Hydrogen peroxide, 93%............	$H_2O_2 \cdot 0,142H_2O$	21,0	1080	1,419	137
Hydrogen peroxide, 87%............	$H_2O_2 \cdot 0,280H_2O$	21,0	927	1,381	126
Isopropyl nitrate..................	$(CH_3)_2CHONO_2$	21,0	990	1,036	169
"	»	70,0	—	»	190
Hydrazine..........................	N_2H_4	25,0	867	1,0085	130
Ethylene oxide.....................	C_2H_4O	20,0	1288	0,887	159,4
	»	60,0	1312	»	180,7
Nitromethane.......................	CH_3NO_2	25,0	2450	1,1286	210*

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[*] In spite of the relatively low sensitivity of nitromethane to various external pulses, attempts to use it as monopropellant led to explosions of great destructive force.

was used as monopropellant for the feed systems of a number of liquid-propellant rocket engines, and also for stabilizing and flight control systems of objects in outer space.

CHAPTER VI

FUNDAMENTALS OF CALCULATIONS OF THERMOCHEMICAL PROPERTIES OF PROPELLANTS

In this section there are examined initial thermochemical properties of propellant, which are subsequently used during selection of propellant and in calculations of combustion and outflow of gases.

§ 1. Calculations on Composition of Propellant Components

For the considered thermochemical calculations of liquid-propellant rocket engines it is not necessary to know the structure of molecules of initial propellant, since the structure of molecules of the final working medium – combustion products, is important when determining the flows of chemically active gases.

Therefore, it is sufficient to determine substances entering the composition of propellant by the quantity of chemical elements entering it. Such propellant composition is called elementary.

In calculation practice there are used two methods of assigning the elementary composition: portion by weight of entering elements g_i (composition by weight) and chemical formula

$$(A_a B_b C_c \ . \ .), \qquad (VI.1)$$

where A, B, C, ... – elements which make up the substance;
a, b, c, ... – number of atoms of elements.

For well studied individual chemical compounds the formulas of substances and their molecular weight are known, for example, nitric acid HNO_3 ($m = 63$), hydrazine N_2H_4 ($m = 32$), etc. Formula (VI.1) is usually written for one mole of substance and is called <u>molecular chemical formula</u>.

If propellant components or the entire propellant are assigned by elementary composition by weight g_i and the molecular weight is unknown for it, then an equivalent chemical formula $(A_a, B_b, C_c \ldots)$ is written for conditional molecular weight $m = 100$, proceeding from relationship

$$\left.\begin{aligned} a = \frac{g_A}{m_A} m = \frac{g_A}{m_A} 100, \\ b = \frac{g_B}{m_B} m = \frac{g_B}{m_B} 100 \\ \cdots\cdots\cdots\cdots \\ \cdots\cdots\cdots\cdots \end{aligned}\right\} \qquad \text{(VI.2)}$$

where m_A; m_B – atomic weights of elements.

Thus, for example, for kerosene with elementary composition, containing carbon $g_C = 86.7\%$ and hydrogen $g_H = 13.3\%$, with conditional molecular weight $m = 100$ we will obtain

$$c = \frac{g_C}{m_C} 100 = \frac{0.867}{12} 100 = 7.225,$$

$$h = \frac{g_H}{m_H} 100 = \frac{0.133}{1} 100 = 13.3.$$

Consequently, the unknown molecular formula for kerosene according to equation (VI.I) will be $C_c H_h = C_{7.225}H_{13.3}$.

In certain cases for convenience of calculation all computations are performed not for a mole, but for 1 kg of propellant. Then instead of molecular formula there is written the specific chemical formula of substance

$$(A_{\bar a}\ B_{\bar b}\ C_{\bar c}\ D_{\bar d}\ \dots). \qquad \text{(VI.3)}$$

Indices $\bar a, \bar b, \bar c, \bar d \dots$ in formula (VI.3) differ m times from corresponding indices in equation (VI.1)

$$\frac{a}{\bar a} = \frac{b}{\bar b} = \frac{c}{\bar c} = \frac{d}{\bar d} = m. \qquad \text{(VI.4)}$$

During calculations of these indices by elementary composition by weight, instead of (VI.2) we use relationships

$$\bar a = \frac{g_A}{m_A}; \quad \bar b = \frac{g_B}{m_B}.$$

Thus, for kerosene with elementary composition $g_C = 86.7\%$ and $g_H = 13.3\%$ we will obtain

$$\bar c = \frac{g_C}{m_C} = \frac{0,867}{12} = 0,07225 \frac{\text{kg-atom}}{\text{kg}} = 72,25 \frac{\text{g-atom}}{\text{kg}},$$
$$\bar{\text{н}} = \frac{g_H}{m_H} = \frac{0,133}{1} = 0,133 \frac{\text{kg-atom}}{\text{kg}} = 133 \frac{\text{g-atom}}{\text{kg}}.$$

Consequently, the unknown specific formula for 1 kg of kerosene according to (VI.3) will be $C_{\bar c}H_{\bar{\text{н}}} = C_{0,07225}H_{0,133}$, where indices signify the number of kg of atoms of carbon and hydrogen in 1 kg of kerosene, or $C_{\bar c}H_{\bar{\text{н}}} = C_{72,25}H_{133}$, where indices $\bar c$ and $\bar{\text{н}}$ signify the number of g of atoms.

It is agreed to write specific chemical formulas in such a manner that indices $\bar a, \bar b, \bar c, \dots$ would signify the number of gram atoms of corresponding elements.

Cases are encountered when the propellant or part of it (fuel or oxidizer) are assigned not by elementary composition, but in the form of a blend of substances. Let us assume that the weight content of these substances in the mixture will be g_1, g_2, ... Then for the entire mixture

$$g_1(A_{\bar{a}_1}B_{\bar{b}_1}C_{\bar{c}_1}\ldots)+g_2(A_{\bar{a}_2}B_{\bar{b}_2}C_{\bar{c}_2}\ldots)+\ldots=(A_{\bar{a}}B_{\bar{b}}C_{\bar{c}}\ldots) \qquad (VI.5)$$

or

$$\frac{g_1}{m_1}(A_{a_1}B_{b_1}C_{c_1}\ldots)+\frac{g_2}{m_2}(A_{a_2}B_{b_2}C_{c_2}\ldots)+\ldots=(A_{\bar{a}}B_{\bar{b}}C_{\bar{c}}\ldots).$$

Such a mixture can be determined specific formula $(A_{\bar{a}}B_{\bar{b}}C_{\bar{c}}\ldots)$, where the value of indices is calculated by the following relationships:

$$\left.\begin{array}{l}\bar{a}=g_1\bar{a}_1+g_2\bar{a}_2+\ldots+g_n\bar{a}_n;\\ \bar{b}=g_1\bar{b}_1+g_2\bar{b}_2+\ldots+g_n\bar{b}_n\\ \cdots\cdots\cdots\cdots\cdots\end{array}\right\} \qquad (VI.6)$$

or

$$\left.\begin{array}{l}\bar{a}=g_1\frac{a_1}{m_1}+g_2\frac{a_2}{m_2}+\ldots+g_n\frac{a_n}{m_n};\\ \bar{b}=g_1\frac{b_1}{m_1}+g_2\frac{b_2}{m_2}+\ldots+g_n\frac{b_n}{m_n}\\ \cdots\cdots\cdots\cdots\cdots\end{array}\right\} \qquad (VI.7)$$

With various writings of equivalent chemical formulas the conditional molecular weight of the substance or mixture of substances is calculated so:

$$m=m_A a+m_B b+m_C c+m_D d+\ldots \qquad (VI.8)$$

or

$$m=\frac{a}{\bar{a}}=\frac{b}{\bar{b}}=\frac{c}{\bar{c}}=\ldots.$$

It is not difficult to note that the specific formula can be considered as the equivalent molecular formula with conditional molecular weight equal to 1 (in kilograms) or 1000 (in grams).

Let us consider some examples on calculation of propellant composition.

Example VI.1. Calculate coefficients in the specific formula of nitric acid, molecular formula of which HNO_3 is well known, and molecular weight is equal to 63.

According to (VI.4) indices in the specific formula will be

$$\bar{a} = \frac{a}{m} = \frac{1}{63} = 0{,}01586;$$

$$\bar{b} = \frac{b}{m} = \frac{1}{63} = 0{,}01586;$$

$$\bar{c} = \frac{c}{m} = \frac{3}{63} = 0{,}0476.$$

Thus, specific formula for one gram of nitric acid $(A_{\bar{a}}B_{\bar{b}}C_{\bar{c}}\ldots)$ will be written so: $H_{0.01586}N_{0.01586}O_{0.0476}$, and for 1 kg $(H_{15.86}N_{15.86}O_{47.6})$.

Example VI.2. Formulate the specific formula of 96% nitric acid. Molecular weights: $m_{HNO_3}=63$ and $m_{H_2O}=18$. Molecular formulas: nitric acid – HNO_3 and water – H_2O.

By equation (VI.7) accordingly for hydrogen, nitrogen, and oxygen we obtain:

$$\bar{a} = 0{,}96\frac{1}{63} + 0{,}04\,\frac{2}{18} = 0{,}01963;$$

$$\bar{b} = 0{,}96\frac{1}{63} + 0 = 0{,}01523;$$

$$c = 0{,}96\frac{3}{63} + 0{,}04\,\frac{1}{18} = 0{,}0479.$$

Specific formula for 1 g of 96% solution of nitric acid and water will be written so $(H_{0.01953}N_{0.01523}O_{0.0479})$, and for 1 kg $(H_{19.63}N_{15.23}O_{47.9})$.

Example VI.3. Formulate the equivalent formula for complex solid rocket propellant, prescribed by the following composition:

Substance	Chemical formula	Part of weight	Molecular weight
1. Nitrocellulose	$C_6H_7O_2(ONO_2)_3$	$0{,}515 = g_1$	297
2. Nitroglycerine	$C_3H_5(ONO_2)_3$	$0{,}430 = g_2$	227
3. Diethyl phthalate	$C_6H_4(COOC_2H_5)_2$	$0{,}0325 = g_3$	222
4. Centralite	$C_{17}H_{20}ON_2$	$0{,}0225 = g_4$	268

Let us first consider the composition of the specific formula of this propellant in the form $C_{\bar{a}}, H_{\bar{b}}, O_{\bar{c}}, N_{\bar{d}}$.

By equation (VI.7) for carbon, hydrogen, oxygen and nitrogen respectively,

$$\bar{a} = 0{,}515 \frac{6}{297} + 0{,}43 \frac{3}{227} + 0{,}0325 \frac{12}{222} + 0{,}0225 \frac{17}{268} =$$

$$= 0{,}0193 \frac{\text{g-atom}}{\text{g}} = 19{,}3 \frac{\text{g-atom}}{\text{kg}},$$

$$\bar{b} = 0{,}515 \frac{7}{297} + 0{,}43 \frac{5}{227} + 0{,}0325 \frac{14}{222} + 0{,}0225 \frac{20}{268} =$$

$$= 0{,}0253 \frac{\text{g-atom}}{\text{g}} = 25{,}3 \frac{\text{g-atom}}{\text{kg}},$$

$$\bar{c} = 0{,}515 \frac{11}{297} + 0{,}43 \frac{9}{227} + 0{,}0325 \frac{4}{222} + 0{,}0225 \frac{1}{268} =$$

$$= 0{,}03676 \frac{\text{g-atom}}{\text{g}} = 36{,}76 \frac{\text{g-atom}}{\text{kg}},$$

$$\bar{d} = 0{,}515 \frac{3}{297} + 0{,}43 \frac{3}{227} + 0{,}0325 \frac{0}{222} + 0{,}0225 \frac{2}{268} =$$

$$= 0{,}011 \frac{\text{g-atom}}{\text{g}} = 11 \frac{\text{g-atom}}{\text{kg}}.$$

Specific formula for 1 g of propellant

$$A_{\bar{a}} B_{\bar{b}} \ldots = C_{0{,}0193} H_{0{,}0253} O_{0{,}03676} N_{0{,}011}.$$

For 1 kg of propellant

$$A_{\bar{a}} B_{\bar{b}} = C_{19{,}3} H_{25{,}3} O_{36{,}7} N_{11}.$$

§ 2. Stoichiometric Ratio Between Propellant Components

Calculations of propellant composition lead to determination of the ratios between combustible and oxidizing elements. As one such ratio there is introduced the idea of stoichiometric composition.

The idea of stoichiometric composition is conditional theoretical, which assumes that the numerical ratio between combustible and oxidizing elements must satisfy equations of those chemical reactions, in which there is accomplished complete oxidation of carbon C to CO_2, hydrogen H to H_2O, etc. With this is assumed the use of total valences of elements, which they can manifest under rocket engine conditions. Valences of chemical elements, encountered in propellants of liquid-propellant rocket engines, are listed in Table VI.1 [27].

Table VI.1.

Element	Atomic weight	Valence	Element	Atomic weight	Valence
H	1,008	—1	Na	22,997	—1
He	4,003	0	Mg	24,320	—2
Li	6,940	—1	Al	26,970	—3
Be	9,200	—2	Si	28,060	—4
B	10,820	—3	P	30,980	—5
C	12,010	—4	S	32,066	—6
N	14,008	—	Cl	35,457	+1
O	16,000	+2	Ar	39,944	0
F	19,000	+1	K.	39,096	—1
Ne	20,183	0			

With separate fuel feed systems to the liquid-propellant rocket engine propulsion systems, when along various hydraulic ducts oxidizer (with the preferential content of oxidizing elements) and fuel (with predominance of reducing elements) are introduced to the combustion chamber, the problem of determining the stoichiometric composition of propellant is reduced to calculation of the stoichiometric ratio between oxidizer and fuel:

$$\chi_0 = \frac{\text{mass (weight) flow rate of oxidizer}}{\text{mass (weight) flow rate of fuel}}. \qquad \text{(VI.9)}$$

In combustion chambers, using solid propellants (RDTT, gas generators in fuel feed systems and so forth) or liquid monopropellant, when there is no separate feed, the stoichiometric ratio between oxidizing and reducing elements of such propellant is calculated analogously to conditional division of fuel into two parts.

Value of x_0 can be determined by formula of substitution of valences of elements in the following way:

a) with use of specific chemical formulas

$$\chi_0 = -\frac{(\Sigma\Delta_i\nu_i)_{\text{гор}}}{(\Sigma\Delta_i\nu_i)_{\text{окисл}}}\ \frac{\text{kg oxidizer}}{\text{kg fuel}}\ ; \qquad \text{(VI.10)}$$

b) with use of molecular formulas of substances

$$\chi_0 = -\frac{m_{\text{окисл}}(\Sigma\Delta_i\nu_i)_{\text{гор}}}{m_{\text{гор}}(\Sigma\Delta_i\nu_i)_{\text{окисл}}}\ \frac{\text{kg oxidizer}}{\text{kg fuel}} \qquad \text{(VI.11)}$$

where Δ_i – element valences from Table VI.1, which are taken with their signs (nitrogen is considered neutral and it is possible not to consider it); ν_i – number of gram atoms of elements in conditional chemical formula.

Dimensionality of $\varkappa_0$, calculated by formulas (VI.10) or (VI.11), corresponds to equation (VI.9), although the algebraic sums in the numerator of (VI.10) and (VI.11) are taken in conformity with chemical formulas of propellant, and in the denominator – chemical formulas of oxidizer.

Sometimes in calculations it is more convenient to apply stoichiometric ratio χ_0' with dimensionality $\frac{\text{mole oxidizer}}{\text{mole fuel}}$, which is determined through molecular weight of combustible $m_{\text{г}}$ and oxidizer $m_{\text{о}}$ so:

$$\chi_0' = \chi_0\frac{m_{\text{гор}}}{m_{\text{окисл}}}\ \frac{\text{mole oxidizer}}{\text{mole fuel}} \qquad \text{(VI.12)}$$

§ 3. Excess Oxidant Ratio

Stoichiometric ratio between propellant components is only a theoretical measure during evaluation of the actual propellant composition, which can be selected different from the stoichiometric value for obtaining the necessary results in ZhRD combustion chambers.

The actual ratio between propellant components is estimated in comparison with stoichiometric through excess oxidant ratio α:

$$\chi = \alpha\chi_0;\ \alpha = \frac{\chi}{\chi_0} = \frac{\chi'}{\chi_0}. \qquad \text{(VI.13)}$$

When $\alpha > 1$ the propellant contains excess oxidizer, and when $\alpha < 1$ – excess combustible elements.

For calculations of actual propellant composition the value of α is usually assigned. Then with known value of stoichiometric ratio $\varkappa_0$ or $\varkappa'_0$ it is possible to formulate the conditional chemical formula for bipropellant, in which the assigned value of α is kept.

Molecular formula of bipropellant

$$A_a B_b C_c D_d \ldots \qquad \text{(VI.14a)}$$

where

$$a = a_r + \alpha\chi'_0 a_0;$$
$$b = b_r + \alpha\chi'_0 b_0;$$
$$\cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot$$

Specific formula for bipropellant

$$(A_{\bar a} B_{\bar b} C_{\bar c} D_{\bar d} \ \ldots). \qquad \text{(VI.14b)}$$

where

$$\bar a = \frac{\bar a_r + \chi_0 \alpha \bar a_0}{1 + \alpha\chi_0};$$
$$\bar b = \frac{\bar b_r + \alpha\chi_0 \bar b_0}{1 + \alpha\chi_0}.$$

In these ratios a_r; b_r; c_r or $\bar a_r$; $\bar b_r$; $\bar c_r$... designate the number of gram atoms of elements in corresponding conditional formulas of fuel, and a_0; b_0; c_0... or $\bar a_0$; $\bar b_0$; $\bar c_0$... – in corresponding formulas of oxidizer.

Let us consider the application of formulas (VI.10-VI.14).

Example VI.4. Calculate the actual ratio between components of propellant, consisting of fuel – dimethylhydrazine (molecular formula $C_2H_8N_2$ and molecular weight m_r = 60.1) and oxidizer – 96% nitrogen tetroxide N_2O_4, having 4% humidity. Excess oxidant ratio α = 0.85.

Formulate conditional formula for all the propellant of type $C_aH_bO_dN_e$.

First let us write specific formula for oxidizer, prescribed by parts by weight g_1 = 0.96 (for N_2O_4) and g_2 = 0.04 (for H_2O). According to equation (VI.7)

$$b_o = 0{,}96\,\frac{0}{92} + 0{,}04\,\frac{2}{18} = 0{,}004445\,\frac{\text{g-atom}}{\text{g}}\left(\frac{\text{kg-atom}}{\text{kg}}\right) = 4{,}445\,\frac{\text{g-atom}}{\text{kg}},$$

$$d_o = 0{,}96\,\frac{4}{92} + 0{,}04\,\frac{1}{18} = 0{,}04394 \quad » \quad » \quad = 43{,}94 \quad »$$

$$e_o = 0{,}96\,\frac{2}{92} + 0{,}04\,\frac{0}{18} = 0{,}02086 \quad » \quad » \quad = 20{,}86 \quad »$$

Specific formula for 1 g of oxidizer will be $H_{0,004}O_{0,044}N_{0,021}$. Let us write the molecular formula for oxidizer under the assumption of conditional molecular weight m_o = 100. Then according to equation (VI.8) the molecular formula for oxidizer is $(H_{0,4445}O_{4,394}N_{2,086})$.

Let us make further calculations by molecular formulas. By using data of Table VI.1, by equation (VI.11) let us determine the stoichiometric ratio between oxidizer and fuel

$$\chi_o = -\frac{m_o}{m_r}\cdot\frac{\Delta_C\, a_r + \Delta_H\, b_r + \Delta_o\, d_r + \Delta_N\, e_r}{\Delta_C\, a_o + \Delta_H\, b_o + \Delta_o\, d_o + \Delta_N\, e_o} = -\frac{100}{60{,}1}\times$$

$$\times\frac{(-4)2 + (-1)\cdot 8}{(-1)\,0{,}4445 + 2\cdot 4{,}394};$$

$$\chi_o = -1{,}663\,\frac{-16}{8{,}343} = 3{,}19\ \frac{\text{kg oxidizer}}{\text{kg fuel}}.$$

According to equation (VI.12)

$$\chi_o' = \chi_o\,\frac{m_r}{m_o} = 3{,}19\,\frac{60{,}1}{100} = 1{,}917\ \frac{\text{mole oxidizer}}{\text{mole fuel}}.$$

The real ratio between components according to equation (VI.13)

$$\chi = \alpha\chi_o = 0{,}85\cdot 3{,}19 = 2{,}71\ \frac{\text{kg oxidizer}}{\text{kg fuel}};$$

$$\chi' = 0{,}85\cdot 1{,}917 = 1{,}63\ \frac{\text{mole}}{\text{mole}}.$$

Molecular formula for all bipropellant according to equation (VI.14a)

$$C_a\,H_b\,O_d\,N_e = C_2\,H_{8,75}\,O_{7,44}\,N_{5,52}\,,$$

where

$$a = 2 + 1{,}692 \cdot 0 = 2;$$
$$b = 8 + 1{,}692 \cdot 0{,}4445 = 8{,}75;$$
$$d = 0 + 1{,}692 \cdot 4{,}394 = 7{,}44;$$
$$e = 2 + 1{,}692 \cdot 2{,}086 = 5{,}52.$$

With such written molecular formula the conditional molecular weight of all the bipropellant according to equation (VI.8) turns out to be equal to

$$m = 12{,}01 \cdot 2 + 1{,}008 \cdot 8{,}75 + 16 \cdot 7{,}44 + 14{,}008 \cdot 5{,}52 = 129{,}2.$$

§ 4. Propellant Enthalpy

During calculations of combustion temperature we use total propellant enthalpy, measured by the sum of thermodynamic enthalpy i and chemical energy $O_{\text{хим}}$:

$$I = i + Q_{\text{хим}} = \int_{T_{\text{нач}}}^{T} c_p\,dT + Q_{\text{хим}}. \qquad \text{(VI.15)}$$

Total bipropellant enthalpy with separate feed to the combustion chamber is determined by the sum of fuel and oxidizer enthalpies:

$$\text{for 1 kg} \quad I = \frac{I_{\text{г}} + \varkappa I_{\text{о}}}{1 + \varkappa} \ \text{kcal/kg;} \qquad \text{(VI.16)}$$
$$\text{for 1 mole} \quad I_m = mI \ \text{kcal/mole,}$$

where $I_{\text{г}}$ and $I_{\text{о}}$ – specific enthalpy of fuel and oxidizer; $\varkappa$ – actual ratio between propellant components, $\frac{\text{kg oxidizer}}{\text{kg fuel}}$.

Total enthalpy of fuel, oxidizer or complex monopropellant, being mixtures of various chemical compounds, is computed by enthalpies of component substances and parts by weight g_i:

$$\text{for } 1 \text{ kg } I = \Sigma g_i I_i \text{ kcal/kg.} \qquad \text{(VI.17)}$$

If during mixing of the forming substances outside the propulsion system their mutual dissolution occurs, then it is necessary to consider heats of dissolution, then

$$I = \Sigma g_i I_i \pm \Sigma g_{ip} Q_{ip} \text{ kcal/kg,} \qquad \text{(VI.18)}$$

where Q_{ip} – heat of dissolution of 1 kg of i dissolved substance in complex solvent; g_{ip} – part by weight of i dissolved substance.

In equation (VI.18) summation in the first item is produced by all the substances, and in the second – only by dissolved. The sign in the second item is minus if heat is liberated during dissolution. In reference data the heat of dissolution usually pertains to a kilogram or mole of dissolved substance.

In thermochemical calculations for engines there is introduced the value of enthalpy of propellant components under combustion chamber feed conditions: feed pressure $p_{\text{п}}$ and temperature of propellant before the burner inlet $T_{\text{п}}$. Tabular values of enthalpy in reference data are derived at initial temperature $T_{\text{нач}}$ (0° K, 293° K and so forth) and at pressure in 1 atm.

Conversions of enthalpy to feed conditions are produced by equation

$$I_{T=T_{\text{п}}} = I_{T=T_{\text{нач}}} + \int_{T_{\text{нач}}}^{T_{\text{п}}} c_p\,dT + \frac{1}{427}\,\frac{p_{\text{п}}}{\gamma_{\text{т}}} = I_{T_{\text{нач}}} + \bar{c}_p(T_{\text{п}} - T_{\text{нач}}). \qquad \text{(VI.19)}$$

where $\gamma_{\text{т}}$ – specific gravity of propellant.

Change of enthalpy from pressure for liquid propellants at low pressures is usually not considered, since work of compression of liquid is very small. At high pressures – more than 80-100 atm – calculation is necessary.

If in the fuel feed system there occurs change of state of matter of propellant or it is in tanks in a different phase state than at standard tabular conditions, then taking into account the heat of phase transition r the total enthalpy is determined by formula

$$I = I_{\text{станд}} \pm r, \qquad \text{(VI.20)}$$

when heat r is lost, in equation (VI.20) it is taken with the "minus" sign.

Example VI.5. Determine enthalpy of 96% nitric acid at T = 293°K, if for this temperature there are known: enthalpy of nitric acid I_{HNO_3} = -657 kcal/kg, enthalpy of water I_{H_2O} = -3798 kcal/kg, Q_p = 325 kcal/kg water. With dissolution of H_2O into HNO_3 the heat of dissolution is liberated outside. Then by equation (VI.18)

$$I_{96\%\,HNO_3} = 0{,}96\, I_{HNO_3} + 0{,}04\, I_{H_2O} - 0{,}04\, Q_p =$$
$$= 0{,}96(-657) + 0{,}04(-3798) - 0{,}04 \cdot 325 = -796 \ \frac{\text{kcal}}{\text{kg}}.$$

Example VI.6. Determine the enthalpy of liquid oxygen, entering the combustion chamber at 25 atm in supercooled state to $T_{\text{н}} = 60°\,\text{K}$ (boiling point of oxygen at this pressure $T_{\text{кип}} = 136{,}5°\,\text{K}$).

From tabular data there are known: enthalpy of gaseous oxygen at p = 1 atm and T = 293°K, comprising $I^{293}_{O_2}$ = 0 and heat of vaporization at p = 1 atm and temperature T = 90°K equal to r = 1629 kcal/kg-mole. Heat capacities of oxygen are taken $c_{\text{газ}}$ = 7 and $c_{\text{жидк}}$ = 0.5 kcal/mole·deg.

For construction of calculation diagram let us examine the sequency of transitions:

$$O_{2\,T=293,\ p=1}^{\text{газ}} \xrightarrow{\text{cooling}} O_{2\,T=90,\ p=1}^{\text{газ}} \xrightarrow{\text{condensation}} O_{2\,T=90,\ p=1}^{\text{жидк.}} \xrightarrow{\text{cooling}}$$

$$\xrightarrow{\text{cooling}} O_{2\,T=60,\ p=1}^{\text{жидк.}} \xrightarrow{\text{compression}} O_{2\,T=60,\ p=25}^{\text{жидк.}} .$$

$$I_{90}^{\text{газ}} = I_{293}^{\text{газ}} + c_p(90-293) = 0 - 7\cdot 203 = -1421 \ \text{kcal/mole},$$

$$I_{90}^{\text{жидк.}} = I_{90}^{\text{газ}} - r = -1421 - 1629 = -3050 \ \text{kcal/kg-mole},$$

$$I_{T=60}^{\text{жидк.}} = I_{T=90}^{\text{жидк.}} + c_{\text{жидк}}(60-90) = -3050 - 15 = -3065 \ \text{kcal/kg-mole}.$$

Change of enthalpy of liquid oxygen with increase of pressure from 1 to 25 atm is not considered here, since the work of compression of liquid is very small. Then we derive that

$$I_{\substack{T=60 \\ p=25 \text{ atm}}}^{\text{жидк.}} = -3065 \ \text{kcal/mole} .$$

§ 5. Reference Systems of Total Enthalpies

Numerical values of total enthalpies depend on the accepted reference system, for construction of which it is necessary to agree in connection with initial reference temperature $T_{\text{нач}}$ and initial level of chemical energies of separate substances.

During calculations it is necessary to operate only with the differences or sums of total enthalpies, therefore, selection of initial values for construction of reference system does not have fundamental value, but is dictated only by considerations of convenience of calculations. It is only obligatory that all calculations be performed according to the same reference system of enthalpies.

Let us show two of the most widely occurring methods of determining total enthalpies in the system of A. P. Vanichev, the most extensively distributed in the Soviet Union, and in the system accepted by NASA (the United States).

Initial temperature for reading enthalpy in Vanichev's system will be $T_{\text{нач}} = 293.16^{\circ}K$ ($20^{\circ}C$), and in NASA system $T_{\text{нач}} = 0^{\circ}K$.

In some systems the levels of chemical energies of various substances are read from the levels of chemical energies of such substances as H_2 (gas), N_2 (gas), O_2 (gas), Cl_2 (gas), F_2 (gas), C (graphite of β-modification), Al (crystal) and other metals, and also electron gas (e), which are taken as initial in so-called standard state, i.e., in stable and the most widely occurring natural form.

Subsequently we will use the A. P. Vanichev reference system of enthalpy everywhere.

According to equation (VI.15) total enthalpy I is composed of thermodynamic enthalpy i and chemical energy $Q_{\text{хим}}$:

$$I = i + Q_{\text{хим}}.$$

For all substances at initial temperature it is considered $i_{T_{\text{нач}}} = 0$.

For parent substances in standard state the level of chemical energy at initial temperature is taken equal to zero, i.e.,

$$Q_{\text{хим}}^{293}\left(H_2^{\text{газ}};\ N_2^{\text{газ}};\ \ldots C_{\text{графит}};\ \text{metals and } e\right) = 0.$$

Consequently, total enthalpy for parent substances at initial temperature according to equation (VI.15) also will be equal to zero:

$$I^{293}\left(H_2^{\text{газ}};\ N_2^{\text{газ}};\ O_2^{\text{газ}};\ \ldots C_{\text{графит}};\ \text{metals and } e\right) = 0.$$

Chemical energy of other more complex or simpler substances is determined by comparison with energy levels of parent substances. For this are used experimental data on heats of formations $Q_{\text{обр}}$ of such substances from initial.

For an example let us determine the level of chemical energy and total enthalpy at initial temperature for water, during formation of $H_2O^{\text{пар}}$ from parent substances H_2 and O_2, taken in standard state. It is known that during the formation of steam ($H_2O^{\text{пар}}$) at T = 293°K and constant pressure p = 1 atm there is liberated heat of formation $Q_{\text{обр}}$ = 57,785 kcal/kg·mole H_2O.

Let us consider two states of the same chemical elements (H and O) in the form:

First state	Parent substances	Thermodynamic enthalpy	Chemical energy
$T = 293$	$H_2^{\text{газ}}$ and $0{,}5O_2^{\text{газ}}$	$i = 0$	$Q_{\text{хим}}(H_2^{\text{газ}}; O_2^{\text{газ}}) = 0$
Second state	Formed steam		
$T = 293$	H_2O	$i = 0$	$Q_{\text{хим}}(H_2O^{\text{пар}}) = ?$

If in the first state $Q_{\text{хим}}(H_2^{\text{газ}}; O_2^{\text{газ}}) = 0$, and during transition to second state $Q_{\text{обр}}$ = 57,785 kcal/mole, was liberated outside then it is obvious that the level of chemical energy of the system became lower than zero by the value of liberated heat of formation, i.e.,

$$Q_{\text{хим}\,H_2O^{\text{пар}}} = -Q_{\text{обр}}.$$

Consequently, total enthalpy of vaporous water at initial temperature will be

$$I^{293}_{H_2O^{\text{пар}}} = -Q_{\text{обр}} = -57\,785 \text{ kcal/kg-mole } H_2O^{\text{пар}}.$$

As another example let us determine the level of chemical energy and total enthalpy for atomic hydrogen H during its formation from molecular hydrogen H_2, taken in standard state at initial temperature 293°K. It is known that during formation of atomic hydrogen H at T = 293°K and constant pressure p = 1 atm there is expended heat of formation

$$Q_{\text{обр}} = 52\,081 \text{ kcal/kg-atom H}.$$

By reasoning analogously, we note that during transition of the system from state H_2 to atomic state H the level of chemical energy of the system is increased by the value of accumulated heat, supplied externally. Consequently,

$$I_{H}^{293} = +Q_{обр} = +52\,081 \text{ kcal/kg-atom H.}$$

By generalizing these two examples, it is possible to write that at initial temperature the total enthalpy of the substance can be determined by its heat of formation from <u>parent substances</u> into <u>standard</u> state by equation

$$I^{293} = \pm Q_{обр}^{293}. \qquad \text{(VI.21)}$$

In the process the heat of formation should be determined or referred to the same temperature. The "plus" sign in equation (VI.21) is taken when heat is expended on the formation of substance, and "minus" sign if the system loses heat outside during formation of substance.

At present usually the standard conditions for determination of heat of formation are pressure 1 atm and temperature 20°C (293°K) or 25°C (298°K). Therefore, the Vanichev reference system is convenient in the fact that at initial temperature 293°K the chemical energy of substance is approximately equal to heat of its formation from initial elements taken in standard state, which can be directly obtained experimentally.

Accuracy of contemporary tabular values of total enthalpies is continuously increased, in proportion to improvement of experimental data on heats of formations of substances and heats of chemical reactions, utilized while compiling tabular data. Therefore, for contemporary propellants it is recommended to use tables of thermodynamic functions with the latest data.

§ 6. Calculation of Total Enthalpy by Heats of Reactions

Propellant or its components are often not simple mixtures or solutions of substances, but chemical compounds, for which there cannot be tabular values of total enthalpies and it is impossible to directly determine heats of their formations from standard parent substances, embodied in reference systems of enthalpies, experimentally.

In such cases for calculation of total enthalpies it is necessary to use thermal effects of chemical reactions, including the substance of interest to us and other substances, for which tabular values of total enthalpy are known. For these purposes there are used reactions, in which thermal effects can be determined by experimental means.

Let us write chemical reaction in general form

$$aA + bB + \ldots \rightarrow cC + dD + \ldots$$

Equation of conservation of energy for this reaction at constant pressure and constant temperature will be

$$aI_A + bI_B \equiv cI_C + dI_D \pm Q_{\text{реакц}}. \qquad \text{(VI.22)}$$

Absolute value of thermal effect of reaction in the right side of equation (VI.22) is included with a "plus" sign if in the course of the reaction the heat from reactants is extracted in the direction shown by the pointer, and with "minus" sign, when for realization of such a reaction it is necessary to expend heat outside. Value of thermal effect should refer to the quantity of substance of interest to us, participating in the chemical reaction.

Let us assume that the substance of interest to us will be A and one mole of this substance ($\alpha = 1$) participates in the reaction, then

$$I_A + bI_B = cI_C + dI_D \pm Q \text{ kcal/mole substance } A.$$

whence

$$I_A = cI_C + dI_D - bI_B \pm Q_{\text{реакц}}. \qquad \text{(VI.23)}$$

By this equation we can calculate the value of total enthalpy I_A at any temperature, if at the same temperature there will be known I_C, I_D, I_B and $Q_{\text{реакц}}$.

The example of formation or decomposition of steam $H_2O^{\text{пар}}$ analyzed above according to type of equation (VI.22) will be written:

<u>during formation</u> of $H_2O^{\text{пар}}$

$$I_{H_2}^{293} + 1/2\, I_{O_2}^{293} = I_{H_2O^{\text{пар}}}^{293} + Q_{\text{образ}}^{293};$$

<u>during decomposition</u>

$$I_{H_2O^{\text{пар}}}^{293} = I_{H_2}^{293} + 1/2\, I_{O_2}^{293} - Q_{\text{разл}}^{293}.$$

$$(Q_{\text{разл}} = Q_{\text{образ}})$$

Let us consider one more example.

<u>Example VI.7.</u> Determine total enthalpy of liquid ethyl alcohol at initial temperature 293°K, if its calorific value is known during combustion in oxygen.

Let us introduce the highest calorific value of alcohol C_2H_5OH into calculation with dimensionality $H_в$ kcal/kg·mole of alcohol, determined calorimetrically during its combustion in gaseous oxygen and cooling of combustion products to 20°C with condensation of steam into liquid water.

Then the equation of combustion can be written so:

$$C_2H_5OH^{\text{жидк}} + 3O_2^{\text{газ}} \longrightarrow 2CO_2^{\text{газ}} + 3H_2O^{\text{жидк}}.$$

By equation (VI.23) we obtain

$$I^{293}_{\text{спирта}} = 2I^{293}_{CO_2^{\text{газ}}} + 3I^{293}_{H_2O^{\text{жидк}}} - 3I^{293}_{O_2^{\text{газ}}} + H_{\text{н}} \text{ kcal/mole of alcohol.}$$

It is assumed that total enthalpies at I = 293°K for $CO_2^{\text{газ}}$, $H_2O^{\text{жидк}}$ and $O_2^{\text{газ}}$ are known.

CHAPTER VII

CALCULATIONS OF COMBUSTION AND ESCAPE OF GASES

In Chapter II there were examined thermodynamic fundamentals of gas flows under the assumption that properties of gases were prescribed by values of their characteristics in the form of gas constant R, heat capacity c_p, adiabatic index k and so forth, and thermal effects were calculated by changes of thermodynamic potentials (enthalpy, entropy and so forth) or were estimated by introduction of conditional polytropic process with some average index n.

During calculations of these characteristics for gaseous combustion products and during the study of flows of chemically active gases in the high temperature region it is necessary to consider phenomenon of dissociation and recombination of molecules. In certain cases attention is also drawn to possible ionization.

Let us elaborate on some methods of such calculations.

§ 1. Concept of Equilibrium Composition of Gases

Process of accomplishment of some reaction of two substances X and Y with formation of substance Z, if the reaction proceeds in one direction, can be written in the form $X + Y \rightarrow Z$. This equation determines dynamics of the process, i.e., the absence of equilibrium.

If such a reaction is fully completed, then there would set in classic equilibrium of one substance Z. In case of cessation of reaction for some reason on one of the stages the classic equilibrium of the composition would be designated by the sum, including the content of three substances

$$X + Y + Z.$$

In chemically active gases of liquid-propellant rocket engines the dissociation reactions are not ceased, but always proceed simultaneously both in forward and inverse directions with the formation of end products and their simultaneous disintegration into component parts

$$X + Y \rightleftarrows Z.$$

If in the combustion chamber of a liquid-propellant rocket engine there would occur one unique reaction of dissociation, written in general form so:

$$aX + bY \underset{U^{об}}{\overset{U^{п}}{\rightleftarrows}} cZ + dW, \qquad \text{(VII.1)}$$

where a, b, c, d – coefficients determining the number of moles of reactants, then according to the mass action law the rates of forward and inverse reactions $U^{п}$ and $U^{об}$ will be expressed by formulas:

$$\begin{aligned} U^{п} &= k^{п} C_X^a C_Y^b; \\ U^{об} &= k^{об} C_Z^c C_W^d \end{aligned} \qquad \text{(VII.2)}$$

here C_X, C_Y, C_Z, C_W – concentrations of substances, expressed in moles per unit of volume; $k^{п}$, $k^{об}$ – coefficients of forward and inverse reaction rates.

By reaction rate U we mean change of concentration of reactants in time

$$U = \frac{dC_i}{d\tau}. \qquad \text{(VII.3)}$$

Let us assume that at the beginning of the reaction there were provided conditions for preferential progress in the direction from left to right, with this $U^{п} > U^{об}$. In proportion to increase of concentration of substances Z and W and lowering of concentration X and Y the rate $U^{п}$ will be decreased, and $U^{об}$ will start to be increased. This will lead to the fact that in some time

$$U^{п} = U^{об}. \tag{VII.4}$$

during which the quantity of substances forming by forward reaction will be equal to the quantity of substances disintegrating in the opposite direction.

Under such conditions the concentrations of substances will be constant and chemical equilibrium composition of gases will be established.

In contrast to classic equilibrium (rest, absence of transformations) the state of chemical equilibrium is dynamic, is not connected with cessation of transformations of substances, and only steady state is established, characterized by constancy of concentration of reactants.

From condition (VII.4) it is clear that with the advance of chemical equilibrium there should be the following relationship:

$$\frac{k^{об}}{k^{п}} = \frac{c_x^a c_y^b}{c_z^c c_w^d} = K_c. \tag{VII.5}$$

Value of K_c is called constant of chemical equilibrium. It depends on the type of reaction, pressure, and temperature.

Approximate character of change of the rates of forward and inverse reactions, and also change of concentration of reactants in the process of establishment of chemical equilibrium are shown on Fig. VII.1. Here the letters with a line – $\overline{c}_X$, $\overline{c}_Y$, $\overline{c}_Z$, $\overline{c}_W$ – designate equilibrium values of concentrations.

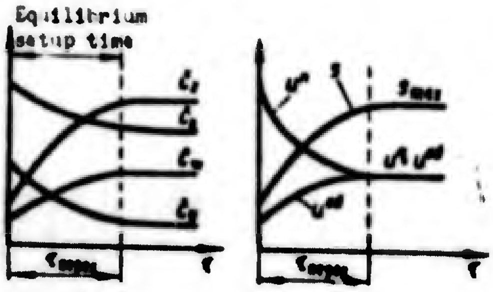

Fig. VII.1. Change of concentrations of reactants in the process of establishment of chemical equilibrium.

On the basis of Fig. VII.1 it may be concluded that, for example, in the combustion chamber of a liquid-propellant rocket engine the equilibrium composition of dissociating combustion products can be established only if the working medium residence time in the chamber column is greater than the duration of transition process, connected with kinetics of chemical transformations.

Furthermore, for achievement of chemical equilibrium still other conditions are necessary:

1. Reactions must be reversible.

2. According to laws of thermodynamics the condition of reversibility requires constancy of entropy of reactants ($ds = 0$).

3. After achievement of chemical equilibrium, equality of chemical potentials of reacting components should set in.

Under the assumption that the enumerated conditions are observed in the combustion chamber and only one reaction of dissociation proceeds there, on the basis of equation (VII.5) the equilibrium composition of gases can be determined unambiguously by the value of equilibrium constant K_c, taken at the pressure and temperature in the chamber.

The question of determination of equilibrium composition of gases, when simultaneously there will proceed several reactions of dissociation and recombination of molecules, mutually affecting each other is more complicated.

Condition of chemical equilibrium in the form of equality of reaction rate in forward and inverse directions $U^{н}=U^{об}$ is strictly substantiated with the help of the second law of thermodynamics only in a particular case, when in the system there occurs a single-unique independent reaction. Let us consider this on the simplest example.

Let us assume that between two states of substances X and Y there can occur mutual transformations both directly $X \rightleftarrows Y$, and through intermediate state Z by means of a chain of reactions

$$X \rightleftarrows Z \text{ and } Z \rightleftarrows Y. \qquad \text{(VII.6)}$$

It is obvious that equilibrium conditions can be satisfied if steady-state value of concentrations of reacting substances is established. Equilibrium can advance both during motion by cycles of Fig. VII.2a and VII.2b (circular one-way course of reactions) and by the cycle of Fig. VII.2c (forward and inverse courses of each reaction).

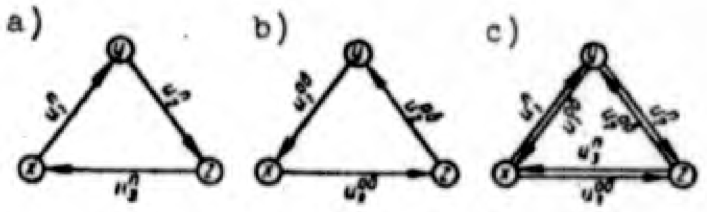

Fig. VII.2. Various possible means of establishment of equilibrium during chemical transformations.

Inasmuch as each reaction has the possibility to some degree of proceeding in forward and inverse directions, then it is possible to consider the diagram of transformations on Fig. VII.2c more general.

So that chemical equilibrium would set in, thermodynamics imposes a unique condition, consisting of achievement of equality of chemical potentials M in all three states of the substance:

$$\overline{M}_x = \overline{M}_y = \overline{M}_z. \qquad \text{(VII.7)}$$

For simplicity let us assume that reactions occur in an ideal system, so that chemical potentials are proportional to logarithms of concentrations:

$$\begin{aligned} M_x &= M_x^0(p;\ T) + RT\ln C_x; \\ M_y &= M_y^0(p;\ T) + RT\ln C_y \\ &\ldots\ldots\ldots\ldots \end{aligned} \qquad \text{(VII.7a)}$$

By placing these equations in condition (VII.7), we obtain

$$\frac{\bar{C}_x}{\bar{C}_y} = k_1; \quad \frac{\bar{C}_y}{\bar{C}_z} = k_2; \quad \frac{\bar{C}_z}{\bar{C}_x} = k_3. \qquad \text{(VII.7b)}$$

Considering Fig. VII.2c, reaction rates according to equation (VII.3) can be written so:

$$\left.\begin{aligned} \frac{dC_x}{d\tau} &= -\left(u_1^{\text{п}} + u_3^{\text{об}}\right) + u_1^{\text{об}} + u_3^{\text{п}}; \\ \frac{dC_y}{d\tau} &= u_1^{\text{п}} - \left(u_1^{\text{об}} + u_2^{\text{п}}\right) + u_2^{\text{об}}; \\ \frac{dC_z}{d\tau} &= u_3^{\text{об}} + u_2^{\text{п}} - \left(u_3^{\text{п}} + u_2^{\text{об}}\right) \end{aligned}\right| \qquad \text{(VII.8)}$$

or, by using relationship VII.2 for reactions of type (VII.2), we obtain

$$\left.\begin{aligned} \frac{dC_x}{d\tau} &= -\left(k_1^{\text{п}} + k_3^{\text{об}}\right)C_x + k_1^{\text{об}}C_y + k_3^{\text{п}}C_z; \\ \frac{dC_y}{d\tau} &= k_1^{\text{п}}C_x - \left(k_1^{\text{об}} + k_2^{\text{п}}\right)C_y + k_2^{\text{об}}C_z; \\ \frac{dC_z}{d\tau} &= k_3^{\text{об}}C_x + k_2^{\text{п}}C_y - \left(k_3^{\text{п}} + k_2^{\text{об}}\right)C_z. \end{aligned}\right| \qquad \text{(VII.9)}$$

In these equations for simplicity the concentrations are written in the first power (it is accepted that indices a = b = c = d = 1).

At equilibrium all derivatives will be equal to zero. On the basis of this taking into account condition (VII.7b) from equation (VII.9) after conversions we will obtain

$$\left.\begin{aligned}\frac{\bar{C}_x}{\bar{C}_y} &= \frac{k_1^{\text{об}}\left(k_3^{\text{п}}+k_2^{\text{об}}\right)+k_2^{\text{п}}k_3^{\text{п}}}{k_1^{\text{п}}\left(k_3^{\text{п}}+k_2^{\text{об}}\right)+k_2^{\text{об}}k_3^{\text{об}}}=k_1;\\ \frac{\bar{C}_y}{\bar{C}_z} &= \frac{k_2^{\text{об}}\left(k_1^{\text{п}}+k_3^{\text{об}}\right)+k_1^{\text{п}}k_3^{\text{п}}}{k_2^{\text{п}}\left(k_1^{\text{п}}+k_3^{\text{об}}\right)+k_1^{\text{об}}k_3^{\text{об}}}=k_2.\end{aligned}\right\} \qquad \text{(VII.10)}$$

If there occurs a particular case of only one reaction proceeding, for example $X \rightleftarrows Y$, then $k_2^{\text{п}}=k_2^{\text{об}}=k_3^{\text{п}}=k_3^{\text{об}}=0$ and from equations VII.8 and VII.9 there can be obtained the earlier written conditions of equilibrium (VII.4) and (VII.5):

$$\frac{k_1^{\text{об}}}{k_1^{\text{п}}}=\frac{\bar{C}_X}{\bar{C}_Y}=k_1;\quad u_1^{\text{п}}=u_1^{\text{об}}.$$

by which concentrations of reactants at equilibrium are simply determined through constants of chemical equilibrium and the rate of forward reaction is equal to the rate in the opposite direction.

If we consider a general case of progress of several reactions, then equations (VII.10) can be satisfied mathematically at many combinations of forward and reverse reaction rates by various means and the equilibrium composition of reactants loses unambiguous character. On this basis it is possible to assume that with approach to chemical equilibrium there will occur oscillations of concentration of reacting components between various "equilibrium" values, satisfying equations (VII.10).

Thus, from the first and second laws of thermodynamics the principle of calculation of equilibrium composition of chemically reacting gases for branching chains of simultaneously proceeding reactions does not follow in evident form.

For foundation of the existing method of calculation of chemical equilibrium an assumption is introduced concerning the fact that in the complex system of reacting gases with approach to chemical equilibrium each separate reaction should be equilibrated, which indicates:

1) transitions by any means in forward and inverse directions must be accomplished equally frequently;

2) condition of equality of rates in forward and inverse directions should always be satisfied for each reaction;

3) concentrations of reacting components upon reaching such detailed balance do not depend on means (on intermediate reactions) by which the system approaches equilibrium, but are determined only by external conditions, which are characterized by pressure and temperature of the reacting gas.

For idealized systems the possibility of such an assumption is based on the quantum theory.

Introduction of this assumption for real systems is very fruitful, it permits calculating the equilibrium composition of gases and analyzing real processes occurring in the combustion chambers and nozzle boxes of liquid-propellant rocket engines. For calculation of equilibrium it is not necessary to return to kinetics of progress of chemical reactions, since the state of equilibrium will not depend on the means of chemical transformations.

§ 2. Equations of Chemical Equilibrium

In connection with the accepted assumptions concerning chemical equilibrium, the composition of gases upon achievement of detailed balance does not depend on the means of reactions, by which this equilibrium is established. Therefore, for calculations of the equilibrium composition of gases it is possible to use chains of reactions and to write equations of dissociation in the form which is the most convenient for calculations.

Let us consider an example of determination of the composition of combustion products of molecular gaseous hydrogen H_2 in oxygen O_2 at detailed chemical equilibrium.

In combustion products there can be the following substances: H_2O, OH, H_2, O_2, H and O. Here molecules H_2O, OH, H_2 and O_2 are complex and can dissociate into simpler molecules and atoms.

For calculations there are often used the following chains of reactions:

$$H_2O \rightleftharpoons H_2 + \frac{1}{2}O_2; \quad H_2O \rightleftharpoons OH + \frac{1}{2}H_2;$$
$$H_2 \rightleftharpoons 2H; \quad O_2 \rightleftharpoons 2O.$$

It is also possible to write dissociation reactions of each complex molecule until attainment of atoms:

$$H_2O \rightleftharpoons 2H + O;$$
$$OH \rightleftharpoons H + O;$$
$$H_2 \rightleftharpoons 2H;$$
$$O_2 \rightleftharpoons 2O.$$

From the point of view of principles of determining chemical equilibrium, both systems of dissociation equations are equally justified. Therefore, subsequently let us agree to use the writing of dissociation reactions of complex molecules to atoms. Such form of writing is simpler and more convenient.

In general form the reaction of dissociation i of complex gas molecule into atoms will be written so:

$$A_{a_i} B_{b_i} C_{c_i} \rightleftharpoons a_i A + b_i B + c_i C \tag{VII.11}$$

or at equilibrium

$$A_{a_i} B_{b_i} C_{c_i} - a_i A - b_i B - c_i C = 0. \tag{VII.12}$$

where $A_{a_i} B_{b_i} C_{c_i}$ – dissociating saturated i molecule; A, B, C – atoms into which the molecule dissociates; a_i, b_i, c_i – coefficients of equation, showing the number of atoms obtained during dissociation.

When writing this equation it is assumed that combustion products are homogeneous gas mixture. With the presence of condensed phases these equations are written in this way with indication of condensed phase by corresponding index $x^{\text{ж}}, x^{\text{тв}}$, which means that the noted substance in calculated conditions (at prescribed temperature) is in liquid or solid state, for example,

$$B_2O_3^{\text{ж}} - 2B - 3O = 0;$$
$$CO_2 + C^{\text{тв}} - 2CO = 0.$$

If at the given temperature some substance can exist in condensed phase, it is necessary to check whether this substance will indeed be present in combustion products in such phase at perceptible concentrations, which must be considered in calculation. This could be judged by the value of chemical equilibrium constant of the examined reaction, which the designated condensed phase enters.

The application of certain propellants in ZhRD propulsion systems can lead to the fact that in combustion products along with predominant gaseous substances there can appear liquid or solid components, such as $B_2O_3^{\text{ж}}$, $Al_2O_3^{\text{тв}}$ and others, having relatively high melting and boiling points.

Under certain conditions of combustion of hydrocarbon propellants there can appear hard carbon.

§ 3. Chemical Equilibrium Constants of Gases

During calculations of the composition of chemically reacting gas mixtures in liquid-propellant rocket engines there are used various methods of determining the concentration of components.

1. By number of moles N_i of each component in the volume of mixture. For ideal gases

$$N_i = p_i\left(\frac{V}{R_\mu T}\right); \quad \frac{N_i}{p_i} = \frac{N_1}{p_1} = \frac{N_2}{p_2} = \ldots = \frac{N_\Sigma}{p_\Sigma}.$$

2. By partial pressures p_i of components of gas mixture.

3. By molar concentration C_i, representing the content of number of moles of i component per unit of volume of mixture:

$$C_i = \frac{N_i}{V} = \frac{p_i}{R_\mu T}.$$

4. By volume (molar) concentration r_i, representing dimensionless ratio of number of moles of i component to number of moles of the entire mixture N_Σ. For ideal gases

$$r_i = \frac{N_i}{N_\Sigma} = \frac{V_i}{V} = \frac{p_i}{p_\Sigma}.$$

With use of chemical equilibrium constants it is necessary to apply them correctly in accordance with the accepted method of assignment of concentration of components of reacting gases.

Taking into account the above-specified writing of equations of equilibrium during dissociation of complex molecules to atoms according to formula (VII.12) the equilibrium constant, expressed through concentration of complex molecule c_i according to equation (VII.5), is written so:

$$k_{c_i} = \frac{c_i}{c_A^{a_i} c_B^{b_i} c_C^{c_i}}. \tag{VII.13}$$

Along with this constant when determining equilibrium composition there are also valid other expressions of equilibrium constants, considering the above-mentioned methods of determining concentration of reacting components:

by partial pressure

$$k_{p_i} = \frac{p_i}{p_A^{a_i} p_B^{b_i} p_C^{c_i}}; \qquad \text{(VII.14)}$$

by number of moles

$$k_{N_i} = \frac{N_i}{N_A^{a_i} N_B^{b_i} N_C^{c_i}}; \qquad \text{(VII.15)}$$

by volume molar concentration

$$k_{r_i} = \frac{r_i}{r_A^{a_i} r_B^{b_i} r_C^{c_i}}. \qquad \text{(VII.16)}$$

In the practice of thermochemical calculations of the composition of gases in liquid-propellant rocket engines preference is given to equilibrium constant k_p, expressed through partial pressures of components by equation (VII.14), since for gases, conforming to equation of state $pV = RT$, the value of this constant does not depend on pressure, but is determined only by type of reaction and temperature of gas. Therefore, we will use only this chemical equilibrium constant and with further designations let us agree to write it through k without index:

$$k = k_p = \frac{p_i}{p_A^{a_i} p_B^{b_i} p_C^{c_i} p_D^{d_i} \ldots}. \qquad \text{(VII.17)}$$

Values of equilibrium constant for dissociation of complex molecules to atoms depending on temperature are given in appendex tables.

With necessity of introduction of other constants k_C, k_N or k_r into calculation let us write their expressions through value of constant:

$$k_C (R_\mu T)^{\Delta\nu} = k; \qquad \text{(VII.18)}$$

$$k_N = k \left(\frac{N_\Sigma}{p_\Sigma} \right)^{\Delta\nu};$$

$$k_p p_\Sigma^{\Delta\nu} = k. \qquad \text{(VII.19)}$$

Here the change of number of moles is designated through $\Delta\nu$. In accordance with equation (VII.12)

$$\Delta\nu = (1 - a - b - \ldots). \qquad \text{(VII.20)}$$

§ 4. Concept of Equilibrium Composition of Heterogeneous Mixture

When among combustion products, except gaseous substances, there are condensed phases (components being in liquid or solid state), then for determination of chemical equilibrium conditions, besides suppositions and conditions stipulated in § 2, it is necessary to introduce more new assumptions, consisting of the following.

1. Condensed particles are so small that they receive the same temperature as gas, i.e., are in thermal equilibrium with gas.

2. The speed of condensed particles is the same as for gas, i.e., they are in dynamic equilibrium with gas flow.

3. Gaseous and condensed phases are not mutually dissolved.

4. Part of the molecules or atoms of condensed substances is always in vaporized state. Partial pressure of these vaporized molecules or atoms is taken equal to the pressure of their saturated vapors, taken at calculated temperature of gas flow. However, as will be shown below, instead of this pressure, in equations of chemical equilibrium constants during heterogeneous reactions there is introduced volatility, equal to one.

5. Partial pressure of the condensed phases themselves is

considered equal to zero.

6. Weight or molar concentration of condensed substances in a number of cases can be considerable, and then it is impossible to disregard it during calculations. However, the specific gravity of condensed phases is approximately 10^3 times greater than gas, therefore, the assumption can be made that the volume of condensed substances is close to zero and it can be disregarded.

It is necessary to consider that the chemical reaction rates in condensed phases are less than reaction rates between gas components. Therefore, the time necessary for establishment of chemical equilibrium in heterogeneous systems considerably increases. Due to this, during the working medium residence time in the combustion chamber or nozzle box of liquid-propellant rocket engines the chemical equilibrium of condensed phases is not established, which will lead to nonequilibrium processes.

§ 5. Chemical Equilibrium Constants of Heterogeneous Reactions

If the melting point and boiling point of the examined i substance, presence of which is assumed in combustion products are relatively high (close to or higher than the gas temperature), then this substance can be in condensed phase and form heterogeneous mixture with gas.

For heterogeneous mixtures of chemically active components equations of equilibrium constants of the heterogeneous reactions, in which the condensed substance enters, must be satisfied.

When some i substance is present in condensed phase, then its partial pressure $p_{i\ \text{конден}}$ in the total heterogeneous mixture is considered equal to the pressure of saturated vapors of this component at the temperature of the entire mixture $p_{i\ \text{насыщ}}=f(T)$.

For solution of the problem of whether this substance will be in condensed form at assigned calculation conditions, it is possible to recommend preliminary calculation of the homogeneous mixture (considering the given component noncondensed) and determination of partial pressure of this substance p_i.

If it turns out that p_i is less than $p_{i\,\text{насыщ}}$, then there will be no condensed phase of i substance and it is possible to be limited by calculation of only homogeneous mixture.

If, however, it is obtained that

$$p_i > p_{i\,\text{насыщ}}, \qquad \text{(VII.21)}$$

then there appear conditions for precipitation of condensed phase of this substance and it is necessary to calculate the chemical equilibrium taking into account the heterogeneous reaction, which the condensed phase enters. Then this calculation will show at what concentrations of other components the content of condensed substance will reach perceptible values, which can affect the qualitative side of liquid-propellant rocket engine operation.

Let us consider the formula for equilibrium constant of heterogeneous reaction on a concrete example.

Let us assume that in combustion products of boron-containing fuels there is B_2O_3, which at the rated temperature can be in condensed state. Then equation (VII.12) of chemical equilibrium with dissociation of B_2O_3 to atoms will be

for homogeneous reaction $B_2O_3 - 2B - 3O = O$;

for heterogeneous reaction $B_2O_3^{\text{конд}} - 2B - 3O = O$.

In the case when B_2O_3 is only in gaseous phase, equilibrium constant of homogeneous reaction $K_{B_2O_3}$ according to this equation

$$K_{B_2O_3} = \frac{p_{B_2O_3}}{p_B^2 p_O^3}.$$

When the reaction will proceed with the presence of condensed phase $B_2O_3^{\text{конд}}$, for heterogeneous reaction

$$K_{B_2O_3} = \frac{p_{B_2O_3}^{\text{конд}}}{p_B^2\, p_O^3}.$$

Here as partial pressure of $p_{B_2O_3}^{\text{конд}}$ one should take the pressure of saturated vapor of B_2O_3, then

$$K_{B_2O_3} = \frac{p_{B_2O_3}^{\text{насыщ}}}{p_B^2\, p_O^3}.$$

In this equation the value of the constant of homogeneous reaction in gas phase $K_{B_2O_3}$ and the pressure of saturated vapor $p_{B_2O_3\,\text{насыщ}}$ do not depend on the concentration of reacting components, but are determined only by temperature, therefore, it is possible to unite them in the form of one <u>constant of heterogeneous reaction</u> $K'_{B_2O_3}$, depending only on temperature:

$$K'_{B_2O_3} = \frac{1}{p_B^2\, p_O^3}. \qquad \text{(VII.22)}$$

With assignment of concentration of reacting components through the number of moles, equation of equilibrium constant of heterogeneous reaction, taking into account equation (VII.19), will be written so:

$$K'_{B_2O_3}\left(\frac{N_{\text{газ.}}}{p_\Sigma}\right)^{\Delta n} = \frac{1}{N_B^2 N_O^3}. \qquad \text{(VII.22a)}$$

Thus, with use of equilibrium constant of heterogeneous reaction $K'_{B_2O_3}$ into equations of constants instead of partial pressure or number of moles of condensed phase there is inserted 1. The value of constant of heterogeneous reaction K' is taken directly by tabular data for equilibrium of condensed substance (B_2O_3 – liquid) or is calculated through the constant of homogeneous reaction of the same substance K taking into account the pressure of saturated vapors of condensed phase.

In this case

$$K'_{B_2O_3} = \frac{K}{p_{B_2O_3\,\text{насыщ}}} . \qquad \text{(VII.23)}$$

By equation of equilibrium constant of heterogeneous reaction it is possible to explain the conditions at which this equation is satisfied and the condensed phase exists.

Thus, for example, with B_2O_3 at gas temperature 2000°K (corresponding to nozzle exit conditions) the equilibrium constant of heterogeneous reaction of dissociation $B_2O_{3\,\text{ж}}$ according to tabular data will be lg K' = 36.002 and absolute value $K = 10^{36}$.

It is obvious that equilibrium equation for condensed phase B_2O_3 according to formula (VII.22)

$$K'_{B_2O_3} = \frac{1}{p_B^2 p_O^3} .$$

will be satisfied when the partial pressure of one of the gaseous components in the denominator becomes very small.

Equilibrium Composition of Gases in the Presence of Ionization

Ionized particles in combustion products of liquid-propellant rocket engines due to thermal ionization appear in noticeable quantities at temperatures over 5000°K. If we disregard the electrostatic interaction between electrically charged particles, then the equilibrium composition of ionized chemically active gas can be determined by the same method as the composition of dissociated gas is calculated. It is necessary to make the assumption that in any sufficiently small volume of gas the total electric charge of electrons and negative ions is equal to the total positive ion charge. Content of ionized particles and electrons can be considered by their partial pressure, by number of moles or by concentration just as for neutral particles.

Let us write some equations of formation of electrically charged particles:

for lithium $Li^+ \rightleftarrows Li - e^-$,

for fluorine $F^- \rightleftarrows F + e^-$,

for nitrogen oxide $NO^+ \rightleftarrows NO - e^-$,

for aluminum (with triple ionization) $Al^{+++} \rightleftarrows Al - 3e^-$.

Equations of ionization constants for these examples will be written so:

for negative ions $K_{ie^-} = \frac{P_{ie^-}}{P_i P_{e^-}}$.

for positive ions $K_{ie^+} = \frac{P_{ie^+} \cdot P_{e^-}}{P_i}$ and $K_{ie^{+++}} = \frac{P_{ie^{+++}} \cdot P^3_{e^-}}{P_i}$.

These constants also depend only on the type of ionization reaction and on gas temperature, as does the constant of dissociation.

During calculations of the content of ionized particles, equations of ionization constants are included in the overall system of equations. For determination of concentration of electrons, this system of equations should include the relationship which determines electrical quasi-neutrality of the flow $Pe^- + \Sigma N_{ie^-} + \Sigma 2N_{ie^{++}} + \ldots = \Sigma N_{ie^+} + \Sigma 2N_{ie^{++}} + \ldots$

§ 6. Calculations for Equilibrium Constants

Systems of equations for calculation of the composition of combustion products include the absolute values of constants of chemical equilibrium K_p and values of partial derivatives $\left(\frac{\partial \ln K_p}{\partial \ln T}\right)$.

Usually in calculations there are introduced tabular values of equilibrium constants, and values of derivatives $\left(\frac{\partial \ln K_p}{\partial \ln T}\right)$ are determined by tabular values of enthalpy of reactants on the basis of Van't Hoff equation

$$\frac{\partial \ln K_p}{\partial T} = -\frac{\Delta I}{RT^2}; \quad \frac{\partial \ln K_p}{\partial \ln T} = -\frac{\Delta I}{RT}. \qquad \text{(VII.25a)}$$

In accordance with the equation of reaction according to formula (VII.12) on the basis of (VII.25a)

$$\left(\frac{\partial \ln K_p}{\partial \ln T}\right)_t = \frac{I_{x_i} - a_i I_A - b_i I_B - c_i I_C \dots}{RT}. \qquad \text{(VII.25b)}$$

With the absence of reliable experimental data on equilibrium constants, recently their calculation by spectroscopic investigations of substances, on the basis of statistical methods[1] and quantum theory, has been widely applied. This method can also be used for reactions taking into account condensed phases.

For calculation of thermodynamic values in quantum theory there is introduced special function Φ, called partition function or simply statistical sum for the given substance:

$$\Phi = \sum g_i \cdot e^{-E_i/kT}. \qquad \text{(VII.25c)}$$

where E_i — energy of molecule in i energy state above the lowest (zero) level. This energy is found by spectroscopic investigation; g_i — relative probability of finding the molecule in i energy level of excitation (quantum weight of state), indicated by quantum mechanics.

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[1] I. N. Godnev. Vychisleniye termodinamicheskikh funktsiy po molekulyarnym uravneniyam (Calculation of thermodynamic functions by molecular equations). Gosgortekhizdat, 1956.

Use of partition function Φ permits calculating any thermodynamic functions.

Usually the partition function Φ is calculated from initial temperature $T_{\text{нач}} = 0°\,K$. At any other initial temperature partition function

$$\Phi' = \Phi + \frac{I_T^0 - I_0^0}{T}, \qquad \text{(VII.25d)}$$

where I_0^0 – enthalpy of substance in standard state at $T_{\text{нач}} = 0°\,K$; I_T^0 – enthalpy of substance in standard state at $T_{\text{нач}} \neq 0°K$.

Having table Φ(T), it is possible to calculate K_p of interesting reaction

$$R \ln K_p = 4{,}57 \lg K_p = \Delta\Phi - \frac{\Delta I_0^0}{T} = \Delta\Phi' - \frac{\Delta I^0_{T\,\text{нач}}}{T}. \qquad \text{(VII.25e)}$$

In addition to values of Φ it is necessary to know only ΔI_0^0 (or $\Delta I^0_{T\,\text{нач}}$): such separation of functions is convenient because Φ(T) for simple gases and well studied solids are found with great accuracy, whereas $\Delta I^0_{T\,\text{нач}}$ is determined from calorimetric data, often less accurate. Thus, any success in determining the value of $\Delta I^0_{T\,\text{нач}}$ can be used for simple conversions of K_p without reconstruction of tables of values of Φ(T).

§ 7. Equations of Conservation of Substance During Chemical Reactions

In calculations the compositions of gases reacting together are based on the law of conservation of substance. This law is applied in the following concrete form: <u>at all chemical transformations of molecules the number of gram atoms of each element does not undergo changes</u>.

Thus, in thermodynamic systems with constant mass of reactants there are preserved equalities of number of gram atoms of each element in the initial propellant (in the initial mixture) and in chemical reaction products at all stages.

Let us assume that the working medium consists of four elements A, B, C, D. Equivalent formula of parent substance of these elements

$$(A_{a_0} B_{b_0} C_{c_0} D_{d_0}).$$

Various chemical compounds, which one or all of these elements can enter, can be written by formula $(A_{a_i} B_{b_i} C_{c_i} \ldots)$, where a_i, b_i, c_i, d_i – number of atoms of each element entering the compound.

Let us assume that $\bar{N}_A$, $\bar{N}_B$, $\bar{N}_C$, $\bar{N}_D$ – number of gram atoms of each element in propellant (in initial mixture). Then equations of balance of each element

$$\begin{aligned} \bar{N}_A &= \sum_{i=1}^{i=n} a_i N_i; \\ \bar{N}_B &= \sum_{i=1}^{i=n} b_i N_i; \\ &\ldots\ldots\ldots\ldots \end{aligned} \tag{VII.26}$$

The number of equations of conservation of elements corresponds to the number of elements in propellant (in initial mixture).

Composition of gases can be calculated from the condition of 1 mole of parent substance (propellant). Then the number of gram atoms of elements in propellant

$$\bar{N}_A = a_0; \quad \bar{N}_B = b_0; \quad \bar{N}_C = c_0; \quad \bar{N}_D = d_0.$$

If calculation is conducted for one kilogram of parent substance,

$$\bar{N}_A = \frac{a_0}{\mu_T}; \quad \bar{N}_B = \frac{b_0}{\mu_T}; \quad \bar{N}_C = \frac{c_0}{\mu_T}.$$

where $\mu_т$ — molecular weight of parent substance.

It is possible to calculate for N_x moles of propellant, then

$$\begin{aligned} N_A &= a_0 N_x; \\ N_B &= b_0 N_x; \\ &\cdots\cdots \end{aligned} \qquad \text{(VII.27)}$$

The quantity of parent substance, for which the composition of gases is calculated, does not have fundamental value. It is expedient to select a quantity of N_x, at which the greatest simplification of calculation formulas is obtained.

The necessity of expressing concentration of reactants in various formulas simultaneously through number of moles N_i and partial pressure p_i imposes considerable inconvenience when performing thermochemical calculations of the composition of gases.

For gases, conforming to equation pv = RT, partial pressures of i component of mixture p_i and its concentration in moles N_i are connected with total pressure p_Σ and number of moles of gases in the mixture N_Σ:

$$\frac{p_i}{N_i} = \frac{p_\Sigma}{N_\Sigma}.$$

The quantity of forming moles of gases N_Σ depends on the number of moles of parent substance N_x, which can be selected from condition

$$\frac{p_\Sigma}{N_\Sigma} = 1, \text{ i.e., } N_\Sigma = p_\Sigma . \qquad \text{(VII.28)}$$

Then for gases

$$p_i = N_i. \qquad \text{(VII.29)}$$

This equality simplifies the writing of formulas and facilitates calculations. Therefore, let us agree to produce thermochemical calculations by determination of composition of gases for N_x moles of parent substance, satisfying condition (VII.28).

When performing calculations for N_x moles of propellant the equation of balance of elements (VII.26) can be written through partial pressures

$$\begin{aligned} \overline{N}_A &= \sum_{i=1}^{i=n} a_i p_i; \\ \overline{N}_B &= \sum_{i=1}^{i=n} b_i p_i; \\ &\cdots\cdots\cdots \end{aligned} \qquad \text{(VII.30)}$$

Before calculations of the composition of gases the number N_x is unknown and it is assigned, proceeding from condition (VII.28). Value of N_x is refined in the course of thermochemical calculations. Generally N_x is introduced into the system of equations for determination of the composition as an additional unknown value, subject to determination in the course of calculation just as other unknown values.

Example 1. Write an equation of balance of elements for the simplest bipropellant, composed of a stoichiometric mixture of fluorine and hydrogen, equivalent formula of which is H_2F_2.

Combustion reaction of this propellant

$$N_x\left(A_{a_x} B_{b_x}\right) \rightarrow N_1\left(A_{a_1} B_{b_1}\right) + N_2\left(A_{a_2} B_{b_2}\right) + N_3\left(A_{a_3} B_{b_3}\right) + \dots,$$

or

$$N_x(H_2F_2) \rightarrow N_{HF}(H_1F_1) + N_{H_2}(H_2F_0) + N_H(H_1F_0) + N_F(H_0F_1).^1$$

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[1] At $T_K = 4500^\circ K$ F_2 is practically completely dissociated.

For the two elements H and F entering the propellant composition, according to (VII.26) and (VII.27) we obtain two balanced equations

$$\overline{N}_H = 2N_x = N_{HF} + 2N_{H_2} + N_H;$$

$$\overline{N}_F = 2N_x = N_{HF} + N_F.$$

Overall number of moles of chemical reaction products

$$N_\Sigma = N_{HF} + N_{H_2} + N_H + N_F.$$

If we perform calculation for N_x moles of propellent, corresponding to conditions (VII.28), then in the obtained equations instead of the number of moles it is possible to write the values of partial pressures, since all components of combustion products will be in gaseous form.

§ 8. System of Equations for Calculation of Equilibrium Composition of Combustion Products at Rated Temperature and Pressure

Let us agree to calculate the composition of combustion products for N_x moles of propellant in accordance with equation (VII.28).

Let us assume that the number of elements entering the composition of parent substances (propellant), is m (m — element propellants).

Content of initial mixture (propellant) is prescribed by conditional formula

$$N_x(A_{a_0} B_{b_0} C_{c_0} D_{d_0} \cdots).$$

For calculations of the equilibrium composition of products of chemical reactions at rated temperature it is not necessary to know in what compounds the chemical elements are found: in initial mixture or in propellant, only the content of these elements is important (A, B, C, D).

We will consider that z substances will be formed from m elements of initial propellant composition after combustion and in the course of reactions of dissociation and possible ionization. Generally, among them will be z_1 electrically neutral molecules and atoms in gaseous form, z_2 electrically neutral molecules and atoms in condensed form, z_3 positive ions, z_4 negative ions and z_{-} free electrons.

Conditional reaction of formation of all these z substances from initial mixture or from propellant taking into account possible ionization will be written in general form:

$$\begin{aligned} N_x(A_{a_0}B_{b_0}C_{c_0}\cdots) \to \sum_{i=1}^{i=z_1} N_i(A_{a_i}B_{b_i}C_{c_i}\cdots) + \\ + \sum_{i=z_1+1}^{i=z_1+z_2} N_i(A_{a_i}B_{b_i}C_{c_i}\cdots)_{\text{конд}} + \sum_{i=z_2+1}^{i=z_2+z_3} N_i(A_{a_i}B_{b_i}C_{c_i}) + \\ + \sum_{i=z_3+1}^{i=z_3+z_4} N_i(A_{a_i}B_{b_i}C_{c_i}) + z_{-}e^{-}. \end{aligned} \qquad \text{(VII.31)}$$

For determination of the composition of reaction products it is necessary to calculate z unknowns, characterizing the concentrations or partial pressures of components (N_i and p_i). Furthermore, as was stipulated in § 7, for simplification of the solution of equations the calculation is performed for earlier unknown N_x moles of parent substances (propellant).

Thus, overall number of unknowns is (z + 1). Therefore, the system of equations for solution of the problem on hand should contain (z + 1) independent equations. Let us consider these equations.

1. Balanced equations of elements:

$$\begin{aligned} a_0N_x &= \sum_{i=1}^{i=z} a_iN_i; \\ b_0N_x &= \sum_{i=1}^{i=z} b_iN_i. \end{aligned} \qquad \text{(VII.32)}$$

The number of these equations is equal to the number of elements m. During calculations for N_x moles of parent substance in these equations for gaseous components instead of N_i it is possible to write p_i, and the value of concentrations N_i always remains for condensed phases; therefore it is better to write system of equations (VII.32) entirely through concentrations N_i.

2. Balanced equation of electrostatic charges during ionization

$$N_{e-} + \sum N_{ie-} + \sum 2N_{ie--} + \ldots = \sum N_{ie+} + \sum 2N_{ie++} + \ldots \qquad \text{(VII.33)}$$

This equation expresses the property of electrostatic equilibrium of ionized gas.

3. Equations of dissociation and ionization in the form of equations of equilibrium constants during calculation for N_x moles of parent substance:

for gases

$$K_i = \frac{p_i}{p_A^{a_i} p_B^{b_i} p_C^{c_i}} = \frac{N_i}{N_A^{a_i} N_B^{b_i} N_C^{c_i}} \qquad \text{(VII.34a)}$$

for condensed substances

$$K'_{i\,\text{конд}} = \frac{1}{p_A^{a_i} p_B^{b_i} p_C^{c_i}} = \frac{1}{N_A^{a_i} N_B^{b_i} N_C^{c_i}}; \qquad \text{(VII.34b)}$$

for positive ions

$$K_{ie+} = \frac{p_{ie+} p_{e-}}{p_i}; \qquad \text{(VII.34c)}$$

for negative ions

$$K_{ie-} = \frac{p_{ie-}}{p_i p_{e-}}. \qquad \text{(VII.34d)}$$

During calculation for 1 mole or 1 kg of propellant these equations are modified in accordance with formulas (VII.15) and (VII.19).

Equations (VII.32), (VII.33) and (VII.34) in totality give a system containing z independent equations. For determination of (z + 1) unknowns this system is supplemented by one more equality.

4. Equation of total number of moles for mixture of components:

$$N_{\Sigma} = \sum_{i=1}^{i=z} N_i \quad \text{(for all substances)} \qquad \text{(VII.35a)}$$

or total pressure of mixture of gas components in Dalton form:

$$p_{\Sigma} = \sum p_i \quad \text{(for all gases).} \qquad \text{(VII.35b)}$$

In accordance with the problem on hand of determination of the equilibrium composition of chemically reacting and ionized mixture of components, for solution of system of equations (VII.32-VII.35) as a necessary and sufficient initial condition there is introduced elementary composition, prescribed by content of chemical elements in propellant or in some initial mixture of intermediate state, i.e., there is assigned: a_0 – content of gram atoms of element A, b_0 – content of gram atoms of element B, etc.

As boundary condition there are considered pressure P and temperature T, at which equilibrium composition is determined.

The examined system has ordinary algebraic equations, part of which (equations of dissociation and ionization) can be nonlinear equations.

Analysis shows that this system of equations is stable, i.e., enabling achievement of solution relative to the sought unknowns.

All possible mathematical solutions which give negative values of partial pressures are rejected, as not having physical meaning. Solutions relative to positive values of sought unknowns are obtained unambiguously, if we exclude imaginary roots.

When the reacting mixture is represented by a small quantity of substances, up to four or five, it is possible to solve the system of equations (VII.32-VII.35) directly by elimination of variables and to obtain analytic expressions for determining the content of components depending on temperature and pressure.

In most complex cases, when the overall number of unknowns is more than five, which is most often the situation with liquid-propellant rocket engines, the attempt of obtaining the final answer will be connected with the necessity of solving not a second or third degree equation, but more complex ones, for which the roots cannot be exactly expressed analytically in the form of known formulas.

Therefore, analytic solutions of system of equations (VII.32) to (VII.35) can be used only for calculation of the simplest cases.

In applied mathematics there is developed an entire series of methods of approximate solution immediately of the entire system of algebraic equations of type (VII.32-VII.35), making it possible to obtain answers with assigned accuracy of calculations. Moreover, the use of approximate methods turns out to be less complex and more convenient, since engineers are always interested only in obtaining results of calculation with the prescribed accuracy.

Usually approximate methods of solution of equations on the mathematical side permit increasing the accuracy of calculations without limit, during which only the volume of calculating work is increased. However, it is necessary to consider the methodical limit of accuracy of calculations, which is limited by the fact that in system of equations (VII.32-VII.35) there are introduced values of equilibrium constants, reliable accuracy of determination of which does not exceed 0.5%. Furthermore, the series of assumptions concerning idealization of working medium properties lowers the authenticity of results of calculations of equilibrium composition by the accepted method still more. Therefore, it makes no sense to require more than 0.5% accuracy from calculating operations.

Practice of calculations of liquid-propellant rocket engines with solution of system of equations (VII.32-VII.35) is based on the method of successive approximations, which is still called the method of iterations (from the Latin word iteratio – repetition).

In reference to calculations of the equilibrium composition of combustion products in liquid-propellant rocket engines on the basis of this method in conjunction with elimination of unknowns, in literature there are described several possible methods and procedures for calculations with the use of a system of solvable equations in a form, such as they are written by formulas (VII.32-VII.35).

Deficiencies of these methods of solutions are the absence of uniformity and limited applicability only for those propellant compositions, on which they are checked. In certain cases it is necessary to change calculation procedures because of the absence of convergence of successive approximations at assigned initial parameters. For these reasons the use of electronic computers for such calculation methods is ineffective.

Recently preference has been given to so-called general method of solution of equations for determination of the equilibrium composition of combustion products, distinguished by the fact that system (VII.32-VII.35) is written in logarithmic form and linearized. Obtained linear system of algebraic equations is solved by the method of successive approximations with respect to corrections, which it is necessary to introduce into subsequent approximations.

In the so-called general method of solution there is improved convergence of approximations, for the most diverse propellant compositions and at various initial parameters there is attained an identical algorithm of finding solutions. This creates a basis for programming the calculations on electronic computers.

Subsequently only this method will be examined.

§ 9. Linearization of Equations for Calculation of Equilibrium Composition of Combustion Products at Rated Temperature and Pressure

Let us write system of equations (VII.32-VII.35) in logarithmic form: balance equations of elements (VII.32)

for atoms A $\lg \sum a_i N_i - \lg a_s N_s = 0;$ (VII.32)'

for atoms B $\lg \sum b_i N_i - \lg b_s N_s = 0;$

. . . .

equation of electrical neutrality for ionized gas (VII.33)

$$\lg [N_{e^-} + \sum N_{k^-} + 2 \sum N_{k^{--}} + \ldots] - \lg [\sum N_{k^+} + 2 \sum N_{k^{++}} + \ldots] = 0; \qquad \text{(VII.33)'}$$

equations of dissociation and ionization (VII.34)

for gases

$$\lg p_i - a_i \lg p_A - b_i \lg p_B - c_i \lg p_C - \ldots - \lg K_i = 0; \qquad \text{(VII.34a)'}$$

equation of overall number of moles:

for condensed substances

$$-a_i \lg p_A - b_i \lg p_B - c_i \lg p_C - \ldots - \lg K'_{i\,\text{конд}} = 0; \qquad \text{(VII.34b)'}$$

for positive ions

$$\lg p_{i+} + \lg p_{e-} - \lg p_i - \lg K_{i+} = 0; \qquad \text{(VII.34c)}'$$

for negative ions

$$\lg p_{i-} - \lg p_{e-} - \lg p_i - \lg K_{i-} = 0; \qquad \text{(VII.34d)}'$$

equations of overall number of moles
for all substances

$$\lg \sum_{1}^{s} N_i - \lg N_{\Sigma} = 0; \qquad \text{(VII.35a)}'$$

for gases

$$\lg \sum_{1}^{s} p_i - \lg p_{\Sigma} = 0. \qquad \text{(VII.35b)}'$$

Solution of system of equations by method of successive approximations is started from some initial approximation of sought unknowns, which are usually assigned. Let us conditionally designate $X_1^0, X_2^0, \ldots, X_i^0$ values of sought quantities during initial approximation.

For linearization of equations (VII.32'-VII.35') in environments of initial approximation let us expand each term of these equations into Taylor series with respect to degrees of deviations

$$F(x_i) = F(x_i)_0 + \left[\frac{\partial F(x_i)}{\partial X_i}\right]_0 \Delta X_i + \text{ nonlinear terms.}$$

Here ΔX_i – deviation of the value of X from the value accepted during initial approximation X_i^0. In logarithmic writing

$$\Delta X_i = X_i - X_i^0;$$

for pressures

$$\Delta \lg p_i = \lg p_i - \lg p_i^0;$$

for concentrations

$$\Delta \lg N_i = \lg N_i - \lg N_i^0;$$

for temperature

$$\Delta \lg T = \lg T - \lg T^0;$$

for number of moles of propellant

$$\Delta \lg N_T = \lg N_T - \lg N_T^0. \qquad \text{(VII.36)}$$

Disregarding the nonlinear terms of expansion, equations of conservation of elements (VII.32) could be written so for element A:

$$\left(\lg \sum a_i N_i\right)_0 + \frac{1}{\left(\sum a_i N_i\right)_0} \sum \left(\frac{\partial (a_i N_i)}{\partial (\lg N_i)}\right)0 \Delta \lg N_i - $$
$$- (\lg a_0 N_T)_0 - \frac{1}{a_0 N_T^0}\left(\frac{\partial (a_0 N_T)}{\partial (\lg N_T)}\right)0 \Delta \lg N_T = 0.$$

For shortening of writing let us introduce the following designations:

$$\left(\lg \sum a_i N_i\right)_0 - \left(\lg a_0 N_T\right)_0 = \delta_A; \qquad \text{(VII.37)}$$

$$\left(\sum a_i N_i\right)_0 = L_A. \qquad \text{(VII.38)}$$

Then equation of conservation of element A will be

$$\sum a_i N_i^0 \Delta \lg N_i - L_A \Delta \lg N_T = -\delta_A L_A. \qquad \text{(VII.39)}$$

Remaining balance equations (VII.32)' and equations (VII.33)' and (VII.35)' will be converted analogously.

Linearization of the group of equations of dissociation and ionization of type (VII.34)' can be considered on an example of equation (VII.34a)' for gases.

After expansion of (VII.34a)' into Taylor series we will obtain

$$(\lg p_i)_0 + \Delta \lg p_i - (a_i \lg p_A)_0 - \left[\frac{\partial (a_i \lg p_A)}{\partial (\lg p_A)}\right]_0 \times$$
$$\times \Delta \lg p_A - (b_i \lg p_i)_0 - \left[\frac{\partial (b_i \lg p_B)}{\partial (\lg p_B)}\right]_0 \Delta \lg p_B - (\lg K_i)_0 -$$
$$- \left[\frac{\partial (\lg K_i)}{\partial (\lg T)}\right]_0 \Delta \lg T = 0.$$

For abbreviation of writing let us designate

$$(\lg p_i - a_i \lg p_A - b_i \lg p_B - \ldots - \lg K_i)_0 = \delta_i; \qquad \text{(VII.40)}$$

$$\left[\frac{\partial (\lg K_i)}{\partial (\lg T)}\right]_0 = L_{K_i}. \qquad \text{(VII.41)}$$

Then equation of dissociation (VII.34a) will take the form

$$\Delta \lg p_i - a_i \Delta \lg p_A - b_i \Delta \lg p_B - c_i \Delta \lg p_C - \ldots -$$
$$- L_{K_i} \Delta \lg T = - \delta_i.$$

If the temperature is assigned exactly from calculation conditions, then the last item $L_{Ki} \Delta \lg T$ can be excluded from the equation. For generality of writing, this term will be kept for the purpose of using system of equations in more complex cases, when the temperature is not assigned, but is subject to determination.

The remaining equations of dissociation and ionization (VII.34b), (VII.34c), (VII.34d) will be converted analogously.

Value of L_K depends on the dissociated substance and temperature. According to Van't Hoff equation

$$L_{K_i} = \left[\frac{\partial (\ln K_i)}{\partial (\ln T)}\right]_0 = \left[\frac{\Delta I}{RT}\right]_0. \qquad \text{(VII.43)}$$

Thermal effect of dissociation of substance ΔI can be taken directly from the tables at rated temperature T_0 or calculated, proceeding from equation of the dissociation of molecules to atoms according to tabular values of heat contents (enthalpies):

$$(\Delta I)_T = (I_i - a_i I_A - b_i I_B - c_i I_C - \ldots). \qquad \text{(VII.44)}$$

Let us now write out the entire system of equations in linear form:

1. Balanced equations of elements:

for atoms A

$$\sum a_i N_i^0 \Delta \lg N_i - L_A \Delta \lg N_x = -\delta_A L_A;$$

$$L_A = \sum a_i N_i^0;$$

$$\delta_A = \lg \sum a_i N_i^0 - \lg a_0 N_x^0; \qquad \text{(VII.45)}$$

for atoms B

$$\sum b_i N_i^0 \Delta \lg N_i - L_B \Delta \lg N_x = -\delta_B L_B;$$

$$L_B = \sum b_i N_i^0; \quad \delta_B = \lg \sum b_i N_i^0 - \lg b_0 N_x^0.$$

2. Equations of electrostatic neutrality during ionization:

$$\frac{1}{L_{e^-}}\left(N_{e^-}^0 \Delta \lg N_{e^-} + \sum N_{ie^-}^0 \Delta \lg N_{ie^-} + 2\sum N_{ie^{--}}^0 \Delta \lg N_{ie^{--}}\right) -$$

$$- \frac{1}{L_{e^+}}\left(\sum N_{ie^+}^0 \Delta \lg N_{ie^+} + 2\sum N_{ie^{++}}^0 \Delta \lg N_{ie^{++}} + \ldots\right) = -\delta_{e^-};$$

$$L_{e^-} = (N_{e^-}^0 + \sum N_{ie^-}^0 + 2\sum N_{ie^{--}}^0 + \ldots);$$

$$L_{e^+} = (\sum N_{ie^+}^0 + 2\sum N_{ie^{++}}^0 + \ldots);$$

$$\delta_{e^-} = \lg (N_{e^-}^0 + \sum N_{ie^-}^0 + 2\sum N_{ie^{--}} + \ldots) - \lg (\sum N_{ie^+}^0 +$$

$$+ 2\sum N^0_{ie^{++}} + \ldots). \qquad \text{(VII.46)}$$

3. Equations of equilibrium during dissociation and ionization:

for gases

$$\Delta \lg p_i - a_i \Delta \lg p_A - b_i \Delta \lg p_B - c_i \Delta \lg p_C - \ldots -$$
$$- L_{K_i} \Delta \lg T = -\delta_i ,$$
$$\delta_i = \lg p_i^0 - a_i \lg p_A^0 - b_i \lg p_B^0 - \ldots - \lg K_i^0 , \qquad \text{(VII.47a)}$$
$$L_{K_i} = \left[\frac{\partial (\lg K_i)}{\partial (\lg T)} \right]_0 = \left(\frac{\Delta I}{RT} \right)_0 ;$$

for condensed substances

$$- a_i \Delta \lg p_A - b_i \Delta \lg p_B - c_i \Delta \lg p_C - \ldots - L_{K_i'} \Delta \lg T = -\delta_k ,$$
$$\delta_k = - a_i \lg p_A^0 - b_i \lg p_B^0 - \ldots - \lg K_i'^0 , \qquad \text{(VII.47b)}$$
$$L_{K_i'} = \left[\frac{\partial (\lg K_i')}{\partial (\lg T)} \right]_0 = \left(\frac{\Delta I}{RT} \right)_0 ;$$

for positive ions

$$\Delta \lg p_{i^+} + \Delta \lg p_{e^-} - \Delta \lg p_i - L_{K_{i^+}} \Delta \lg T = -\delta_{i^+} ;$$
$$\delta_{i^+} = \lg p_{i^+}^0 + \lg p_{e^-}^0 - \lg p_i^0 - \lg K_{i^+}^0 .$$
$$L_{K_{i^+}} = \left[\frac{\partial (\lg K_{i^+})}{\partial (\lg T)} \right]_0 = \left(\frac{\Delta I}{RT} \right)_0 ; \qquad \text{(VII.47c)}$$

for negative ions

$$\Delta \lg p_{i^-} - \Delta \lg p_{e^-} - \Delta \lg p_i - L_{K_{i^-}} \Delta \lg T = -\delta_{i^-} ;$$
$$\delta_{i^-} = \lg p_{i^-}^0 - \lg p_{e^-}^0 - \lg p_i^0 - \lg K_{i^-}^0 ;$$
$$L_{K_{i^-}} = \left[- \frac{\partial (\lg K_{i^-})}{\partial (\lg T)} \right]_0 = \left(\frac{\Delta I}{RT} \right)_0 . \qquad \text{(VII.47d)}$$

for all substances

$$\sum N_i \Delta \lg N_i = -\delta_N N_\Sigma^0 ;$$
$$N_\Sigma^0 = \sum N_i^0 ; \qquad \text{(VII.48a)}$$
$$\delta_N = \lg \sum N_i^0 - \lg N_\Sigma^0 ;$$

for gases

$$\sum p_i \Delta \lg p_i = -\delta_p p_\Sigma^0;$$
$$p_\Sigma^0 = \sum p_i^0;$$
$$\delta_p = \lg \sum p_i^0 - \lg p_K^0. \qquad \text{(VII.48b)}$$

In this system of linear equations corrections $\Delta \lg N_i$, $\Delta \lg p_i$, $\Delta \lg T$, $\Delta \lg N_x$, appear as unknowns, which are subsequently used for improvement of solutions by formulas (VII.36):

for pressures	$\lg p_i' = \lg p_i^0 + \Delta \lg p_i;$
for concentration	$\lg N_i = \lg N_i^0 + \Delta \lg N_i;$
for temperature	$\lg T = \lg T^0 + \Delta \lg T;$
for number of moles of propellant	$\lg N_x = \lg N_x^0 + \Delta \lg N_x.$

Overall number of corrections corresponds to the number of unknowns determining the equilibrium composition of the chemically reacting mixture.

As a rule, calculation of the composition is produced at rated temperature and pressure. In this case as initial approximation for temperature is used its exactly assigned value. Then the term containing $\Delta \lg T$ in equations (VII.47) should be omitted. However, for generality of writing this term is kept in equation (VII.47) for the purpose of using the entire system in more complex cases of calculation, when the temperature is not assigned, but subject to determination.

In almost all calculations, when the combustion temperature is lower than 5000°K, ionization of substances can be disregarded and equations (VII.46) and (VII.47c, d) separated from system (VII.45-VII.48). With the absence of condensed substances equations (VII.47b) are dropped and it is possible to conduct the entire calculation of composition of components for some gaseous substances by partial pressures.

For generality of calculations it is important to establish writings of equations with uniform order and a single algorithm for finding solutions. System n of first degree equations with n unknowns generally has the form

$$\begin{aligned}
&a_{11}x_1 + a_{12}x_2 + a_{13}x_3 + a_{14}x_4 + \ldots + a_{1n}x_n = b_1;\\
&a_{21}x_1 + a_{22}x_2 + a_{23}x_3 + a_{24}x_4 + \ldots + a_{2n}x_n = b_2;\\
&a_{31}x_1 + a_{32}x_2 + a_{33}x_3 + a_{34}x_4 + \ldots + a_{3n}x_n = b_3;\\
&\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\\
&a_{n1}x_1 + a_{n2}x_2 + a_{n3}x_3 + a_{n4}x_4 + \ldots + a_{nn}x_n = b_n.
\end{aligned} \tag{VII.49}$$

Such a system for solutions is assigned in the form of a matrix containing columns of coefficients at unknowns and columns of free terms:

$$\begin{aligned}
&a_{11}a_{12}a_{13}a_{14}\ldots a_{1n}b_1;\\
&a_{21}a_{22}a_{23}a_{24}\ldots a_{2n}b_2;\\
&a_{31}a_{32}a_{33}a_{34}\ldots a_{3n}b_3;\\
&a_{41}a_{42}a_{43}a_{44}\ldots a_{4n}b_4;\\
&\ldots\ldots\ldots\ldots\ldots\\
&a_{n1}a_{n2}c_{n3}a_{n4}\ldots a_{nn}b_n.
\end{aligned} \tag{VII.50}$$

Columns in this matrix are arranged in order of numbers of unknowns x_1. x_2, x_3, x_4, etc. Thus, the third column is assigned under coefficients of equations at the third unknown. Free terms of equations are written in the last column.

In calculated system (VII.45-VII.48) the role of unknowns x_1, x_2, x_3, ..., are played by determinate corrections $\Delta\lg p_i$, $\Delta\lg N_i$, $\Delta\lg N_x$, $\Delta\lg T$, arrangement of which in columns (by ordinal numbers of unknowns) affects the convenience of calculations. Therefore, let us agree to arrange the determined corrections by ordinal numbers of unknowns (by columns of matrix) in the following way:

a) corrections for dissociating neutral molecules of gaseous components;

b) corrections for atomic components;

c) corrections for condensed substances;

d) corrections for ionized components;

e) corrections for number of moles of propellant $\Delta \lg N_{\text{г}}$, then for temperature $\Delta \lg T$ (if it is subject to determination);

f) the last column is assigned for free terms of equations δ.

Equations (VII.45-VII.48) are arranged in matrix rows in the following order:

a) first there are written equations of dissociation of electrically neutral gas molecules (VII.47a) in the same sequence these molecules are arrayed in columns;

b) equations of dissociation of condensed substances (VII.47b) are written in the same sequence as these substances are arrayed in columns;

c) equations of ionization (VII.47c, d);

d) equations of conservation of elements (VII.45) in the same order as they are written in columns;

e) equations of electrical neutrality (VII.46) and equation of overall number of moles (VII.48), or Dalton equation;

f) if the temperature is not assigned, but subject to determination, then as the last row there is added the equation of conservation of enthalpy or entropy, as this will be mentioned below.

§ 10. Formulation of Linearized System of Equations for Determination of Equilibrium Composition of Combustion Products at Rated Temperature and Pressure

Let us consider the simplest example of determining the equilibrium composition of combustion products of a stoichiometric mixture of fluorine F_2 and hydrogen H_2 at temperature $T = 4600^{\circ}K$ and pressure $p_{к} = 25$ atm.

This simple system at rated temperature contains only four components in gaseous combustion products: HF, H_2, H and F. Calculation will be used to determine concentration or partial pressures of these substances. Furthermore, if calculation is performed for earlier unknowns of moles of initial propellant, in order to satisfy condition (VII.29), then the fifth unknown will be the value of N_x.

Such a system of five unknowns, as was shown in § 8, allows the possibility of solving it by means of elimination of unknowns and obtaining final formulas for the content of each substance in evident form, without the application of numerical calculation by the method of successive approximations.

However, this does not hold true for illustration of the general method of solution of a linearized system of equations by the method of successive approximations. General method is useful for determination of any number of unknowns, which it is necessary to encounter in the calculation practice of liquid-propellant rocket engines.

For the considered two-element initial propellant conditional molecular formula $A_{a_0} B_{b_0}$ will be

$$(A_{a_0} B_{b_0}) = (H_2F_2).$$

where $a_0 = 2$ and $b_0 = 2$.

Determined unknowns are distributed in the following way:

Dissociating electrical neutral gas molecules	Atomic electrically neutral gases	Condensed substances	Ionizing substances	Remaining unknowns
x_1 x_2	x_3 x_4	none	none	x_5
$\Delta \lg p_{HF}$ $\Delta \lg p_{H_2}$	$\Delta \lg p_H$ $\Delta \lg p_F$	none	none	$\Delta \lg N_x$

Let us write system of equations (VII.45-VII.48) in the sequence that they will be arranged in calculation matrix rows, adhering to rules of the preceding section.

1. Equilibrium equations in the form of (VII.47a):
for dissociation of HF;

$$x_1 - x_3 - x_4 = -\delta_{HF};$$
$$(A_{a_i} B_{b_i}) = (HF);$$
$$a_i = 1; \quad b_i = 1;$$
$$\delta_{HF} = \lg p^0_{HF} - \lg p^0_H - \lg p^0_F - \lg K^0_{HF}.$$

Here item $L_{K_i} \Delta \lg T$ is omitted, since according to calculation conditions the temperature is assigned and not subject to determination:

for dissociation of H_2;

$$x_2 - 2x_3 = -\delta_{H_2};$$
$$(A_{a_i} B_{b_i}) = (H_2);$$
$$a_i = 2; \quad b_i = 0;$$
$$\delta_{H_2} = \lg p^0_{H_2} - 2 \lg p^0_H - \lg K^0_{H_2}.$$

(Item $L_{K_{H_2}} \Delta \lg T$ is omitted).

2. Balanced equations of elements in the form of (VII.45):
for atoms H:

$$(p^0_{HF}x_1 + 2p^0_{H_2}x_2 + p^0_{H}x_3) - L_H x_5 = -\delta_H L_H;$$
$$L_H = p^0_{HF} + 2p^0_{H_2} + p^0_{H};$$
$$\delta_H = \lg L_H - \lg 2N^0_{\Sigma};$$

for atoms F:

$$(p^0_{HF}x_1 + p^0_{F}x_4) - L_F x_5 = -\delta_F L_F;$$
$$L_F = p^0_{HF} + p^0_{F};$$
$$\delta_F = \lg L_F - \lg 2N^0_{\Sigma}$$

When writing balanced equations of elements it is considered that during calculations for N_x moles of initial propellant on the basis of (VII.29) for gases $p_i = N_i$.

3. Equations of overall number of moles for gases in the form of (VII.48b):

$$p^0_{HF}x_1 + p^0_{H_2}x_2 + p^0_{H}x_3 + p^0_{F}x_4 = -\delta_N p^0_{\Sigma};$$
$$p^0_{\Sigma} = p^0_{HF} + p^0_{H_2} + p^0_{H} + p^0_{F};$$
$$\delta_N = \lg p^0_{\Sigma} - \lg p_K.$$

For solution of this system of equations by the method of successive approximations first there are assigned initial values of sought unknowns p^0_{HF}, $p^0_{H_2}$, p^0_{H}, p^0_{F} and N^0_{Σ} or their logarithms $\lg p^0_{HF}$, $\lg p_{H_2}$, $\lg p^0_{H}$, $\lg p^0_{F}$ and $\lg N^0_{\Sigma}$. Then, by solving the system of equations, we find corrections x_1, x_2, x_3, x_4, and x_5, by which values of sought unknowns are refined according to formulas (VII.36):

$$\lg p'_{HF} = \lg p^0_{HF} + x_1;$$
$$\lg p'_{H_2} = \lg p^0_{H_2} + x_2;$$
$$\cdots\cdots\cdots\cdots$$
$$\lg N'_{\Sigma} = \lg N^0_{\Sigma} + x_5.$$

Refined values of sought unknowns $p'_{HF}, \bar{p}'_{H_2}, p_H, p'_F$ and N'_x are only the first approach to final results.

For further improvement of values of sought unknowns the calculation is repeated, taking instead of $p^0_{HF}, p^0_{H_2}, p^0_H, p^0_F$ and N^0_x the new values obtained after first approximation, namely $p'_{HF}, p'_{H_2}, p'_H, p'_F$ and N'_x. Thus, we proceed until final results of calculations attain the prescribed accuracy of determination of unknowns.

Basic peculiarity of the method of successive approximations consists of the fact that the final solution does not depend on selection of initial values of sought unknowns, which are assigned at the very beginning of calculations.

It is possible to assume initial values of all unknowns equal to zero ($\lg p^0_{HF} = \lg p^0_{H_2} = \lg p^0_H = \lg p^0_F = \lg N^0_x = 0$) or to assign them some tentative values.

Sometimes zero initial values of partial pressures are given only to those substances, whose content in combustion products is supposedly small.

As tentative values, nonzero, it is possible to take values which are found from approximate calculations of combustion without taking dissociation into account or from calculations taking dissociation into account, but performed for other values of temperature and pressure of combustion products of this propellant, close to calculated variant.

Selection of initial approximate values of unknowns affects only the number of operations by successive approximation to the final results.

Another peculiarity of the method of successive approximations consists of the fact that calculation accuracy is increased in proportion to approach to final results. Therefore, at the beginning of calculation it is obligatory to require high accuracy of calculation operations. In the first approximations calculations can be produced with rounding off of signs, and subsequently it is necessary to increase the number of considered signs in each successive approximation to the required accuracy.

In contrast to exact solutions of equations by analytic formulas, in the method of successive approximations the error allowed in the course of calculations of separate figures only increases the time consumption of work.

In the considered example for illustrations of the start of solution identical initial values of partial pressures will be assigned absolutely arbitrarily:

$$p^0_{HF} = p^0_{H_2} = p^0_H = p^0_F = \frac{p_K}{4} = \frac{25}{4} = 6{,}25$$

or their logarithms

$$\lg p^0_{HF} = \lg p^0_{H_2} = \lg p^0_H = \lg p^0_F = \lg 6{,}25 \approx 0{,}8.$$

Conditional reaction of formation of combustion products from propellant through number of moles

$$N_x(H_2F_2) \to N_{HF} + N_{H_2} + N_F + N_H.$$

In order to satisfy condition (VII.29), with which for gaseous products $N_x = p_\Sigma$ and $N_i = p_i$, it is necessary to calculate the number of moles of initial propellant N_x, at which the weight of combustion products will be equal to the weight of taken propellant. This is carried out at condition

$$N_x \mu_{H_2F_2} = N_{HF}\mu_{HF} + N_{H_2}\mu_{H_2} + N_H\mu_H + N_F\mu_F. \qquad \text{(VII.51)}$$

or

$$N_x \mu_{H_2F_2} = p_{HF}\mu_{HF} + p_{H_2}\mu_{H_2} + p_H\mu_H + p_F\mu_F.$$

whence it is possible to estimate initial value

$$N_x^0 = \frac{p_{HF}^0 \mu_{HF} + p_{H_2}^0 \mu_{H_2} + p_H^0 \mu_H + p_F^0 \mu_F}{\mu_{H_2F_2}} =$$

$$= \frac{6,25\,(20 + 2 + 1 + 19)}{40} = 6,5\,.$$

For calculations let us write out tabular values of equilibrium constants for dissociation of molecules to atoms. At the rated combustion temperature 4600°K they will be equal to

$$\lg K_{HF} = 0,116 \text{ and } \lg K_{H_2} = -1,19.$$

For writing the system in general form of type (VII.49) we will calculate free terms and coefficients of equations for the first approximation:

$$b_1 = -\delta_{HF} = -\left(\lg p_{HF}^0 - \lg p_H^0 - \lg p_F^0 - \lg K_{HF}^0\right) =$$

$$= -(0,8 - 0,8 - 0,8 - 0,116) = 0,916;$$

$$b_2 = -\delta_{H_2} = -\left(\lg p_{H_2}^0 - 2\lg p_H^0 - \lg K_{H_2}^0\right) =$$

$$= -(0,8 - 2\cdot 0,8 + 1,19) = -0,39;$$

$$L_H = (p_{HF}^0 + 2p_{H_2}^0 + p_H^0) = 6,25 + 2\cdot 6,25 + 6,25 = 25;$$

$$\delta_H = \lg L_H - \lg 2N_x^0 = \lg 25 - \lg 2\cdot 6,5 = 0,283;$$

$$b_3 = -\delta_H L_H = -0,283\cdot 25 = -7,08;$$

$$L_F = (p_{HF}^0 + p_F^0) = 6,25 + 6,25 = 12,5;$$

$$\delta_F = \lg L_F - \lg 2N_x^0 = \lg 12,5 - \lg 2\cdot 6,5 = -0,017;$$

$$b_4 = -\delta_F L_F = 0,017\cdot 12,5 = 0,2125;$$

$$p_\Sigma^0 = p_{HF}^0 + p_{H_2}^0 + p_H^0 + p_F^0 = 25;$$

$$\delta_N = \lg p_\Sigma^0 - \lg p_\kappa = \lg 25 - \lg 25 = 0;$$

$$b_5 = -\delta_N p_\Sigma^0 = 0.$$

Let us write the entire system of equations in the form of matrix of coefficients (VII.50) for finding corrections (for an example calculation of fluorine and hydrogen combustion). First approximation

Designation of equations	Dissociated molecules		Atomic substances		Remaining unknowns	Free terms
	x_1	x_2	x_3	x_4	x_5	e
	$\Delta \lg p_{HF}$	$\Delta \lg p_{H_2}$	$\Delta \lg p_H$	$\Delta \lg p_F$	$\Delta \lg N_{\Sigma}$	
Dissociation of HF .	1	0	—1	—1	0	0,916
Dissociation of H_2 .	0	1	—2	0	0	—0,39
Balance of atoms H .	6,25	12,5	6,25	0	—25	—7,08
Balance of atoms F. .	6,25	0	0	6,25	—12,5	0,21
Total number of moles (Dalton equation)	6,25	6,25	6,25	6,25	0	0

Let us consider the solution of such a system by the matrix method with the aid of methods of linear algebra.

In the written matrix the accepted distribution of unknowns (by columns) and equations (by rows) permits obtaining a unit matrix in the upper left corner, which gives the possibility in the course of calculations of eliminating part of the unknowns.

§ 11. General Method of Solution of the System of Equations for Calculation of the Composition of Combustion Products

General method is distinguished by the fact that initial matrix of coefficients (VII.50) is preliminarily broken down into diagram

$$\left\| \begin{array}{c|c} U_m & a_1 \\ \hline a_2 & a_3 \end{array} \right\|. \qquad \text{(VII.52)}$$

Separated unit matrix U_m has order equal to the number of dissociating electrically neutral molecules of gas m.

The presence of unit matrix U_m permits excluding m unknowns, relating to dissociation molecules of gas $(x_1, x_2, \ldots, x_m, \ldots)$, and compiling determinant $|a_4|$ for calculation of the remaining unknowns $(x_{m+1}; x_{m+2}, \ldots, x_n)$ for formula

$$\left| a_4 \right| = \left| a_3 \,\vdots\, a_5 \right| \times \left| \frac{-a_1}{U_k} \right|. \qquad \text{(VII.53)}$$

where U_K – unit determinant with order equal to the number of columns of determinant $|-a_1|$.

To matrix $|a_4|$ there is applied solution by the method of inverse substitution of auxiliary determinant and there are found all unknowns, except partial pressures (concentrations) of dissociating molecules of gases.

After finding corrections $(x_{m+1}, x_{m+2}, \ldots, x_n)$, the initially eliminated unknowns $(x_1, x_2, \ldots, x_m)$ are determined by formula

$$\begin{vmatrix} x_1 \\ x_2 \\ \cdots\cdot \\ x_m \end{vmatrix} = \left| -a_1 \right| \cdot \begin{vmatrix} x_{m+1} \\ x_{m+2} \\ \cdots\cdot \\ x_n \\ -1 \end{vmatrix} \qquad \text{(VII.54)}$$

In literature on the method of calculations of liquid-propellant rocket engines there is not covered analysis of mathematical conditions at which in the examined general method of calculations of composition of combustion products there is attained absolute convergence of solutions during successive approximations. However, extensive practice of calculations by this method shows convergence of solutions for all the known compositions of propellant used in liquid-propellant rocket engines. Besides it is noted that in the case of a large number of unknowns (over 12-15) final calculation results are attained with a smaller number of approximations than at other known methods of solution of such equations.

Since it is necessary to expend much time on solution of the system of these equations, let us consider a numerical example on determination of the composition of combustion products of fluorine F with hydrogen H at temperature T = 4600°K and pressure p_K = 25 atm.

Initial matrix of coefficients of equations for the first approximation was obtained in the preceding paragraph. After breaking down this matrix by formula (VII.52) let us write the expression of intermediate determinant (α_4) by equation (VII.53):

$$|\alpha_4| = \begin{vmatrix} 6,25 & 12,5 & 6,25 & 0 & -25 & -7,08 \\ 6,25 & 0 & 0 & 6,25 & -12,5 & 0,21 \\ 6,25 & 6,25 & 6,25 & 6,25 & 0 & 0 \end{vmatrix} \times \left|\begin{array}{cccc} 1 & 1 & 0 & -0,916 \\ 2 & 0 & 0 & +0,39 \\ \hdashline 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{array}\right|$$

So that it would be possible to multiply matrices $|\alpha_4|$, the number of columns of determinant $|\alpha_2|\alpha_3|$ and number of rows of determinant $\left|\frac{-\alpha_1}{U_K}\right|$ must be equal. If this is not observed, then in unit determinant U_K there can be added an empty row, which is filled with zeros.

Product of matrices is calculated in a certain way – by element multiplication of row of determinant $|\alpha_2|\alpha_3|$ by the corresponding column of determinant $\left|\frac{-\alpha_1}{U_K}\right|$ and summation.

If we designate the product of matrices through

$$|E| = \begin{vmatrix} e_{11} & e_{12} & e_{13} & e_{14} \\ e_{21} & e_{22} & e_{23} & e_{24} \\ e_{31} & e_{32} & e_{33} & e_{34} \\ \cdot\ \cdot\ \cdot & \cdot\ \cdot & \cdot\ \cdot & \end{vmatrix},$$

then multiplication of the first row $|\alpha_2|\alpha_3|$ by the first column $\left|\frac{-\alpha_1}{U_K}\right|$

gives e_{11}:

$$(6{,}25\cdot 1) + (12{,}5\cdot 2) + (6{,}25\cdot 1) + (0\cdot 0) + (-25\cdot 0) + (-7{,}08\cdot 0) = 37{,}5;$$

multiplication of the second row $|a_2 : x_3|$ by the first column $\left|\frac{-e_1}{U_x}\right|$ gives e_{21}:

$$(6{,}25\cdot 1) + (0\cdot 2) + (0\cdot 1) + (6{,}25\cdot 0) + (-12{,}5\cdot 0) + (0{,}21\cdot 0) = 6{,}25$$

multiplication of the first row $|a_2 : a_3|$ by the second column $\left|\frac{-x_1}{U_x}\right|$ gives e_{12}:

$$(6{,}25\cdot 1)+(12{,}5\cdot 0)+(6{,}25\cdot 0)+(0\cdot 1)+(-25\cdot 0)+(-7{,}08\cdot 0) = 6{,}25,$$ etc.

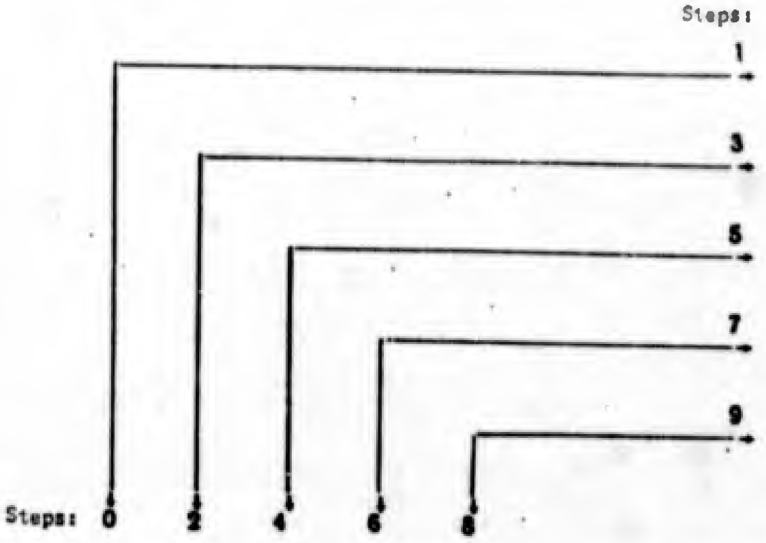
Let us write out the intermediate matrix $|x_4|$ completely:

$$|a_4| = \left|\begin{array}{cccc} x_3 & x_4 & x_5 & \text{Free terms} \\ 37{,}5 & 6{,}25 & -25 & -7{,}92 \\ 6{,}25 & 12{,}5 & -12{,}5 & -5{,}51 \\ 25 & 12{,}5 & 0 & -3{,}28 \end{array}\right|$$

Thus, part of the unknowns, relating to content of dissociating molecules of gas (x_1 and x_2), is eliminated. Obtained intermediate system is solved by the method of reverse substitution. For this purpose there is formulated auxiliary determinant $|x_5|$ of the same order as $|x_4|$. Let us designate this determinant:

$$|a_5| = \left|\begin{array}{cccccc} C_{11} & C_{12} & C_{13} & \ldots & C_{1n} & g_1 \\ C_{21} & C_{22} & C_{23} & \ldots & C_{2n} & g_2 \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ C_{n1} & C_{n2} & C_{n3} & & C_{nn} & g_n \end{array}\right| \qquad \text{(VII.55)}$$

Auxiliary determinant $|x_5|$ in equation (VII.55) is filled in the following order: first there is written out the first column from basic matrix $|a_4|$ without changes then elements of the first row are calculated, then elements of the second column, starting from the leading diagonal, which connects all points of intersection of lines downward, then the second row from the leading diagonal to the right, further the third column from the diagonal downward, third row to the right and so on until the entire determinant is filled in (see diagram).



Calculation of elements of auxiliary determinant (VII.55) is produced so:

$$C_{ij} = a_{ij} - (C_{i1}a_{1j} + C_{i2}a_{2j} + C_{i3}a_{3j} + \dots), \qquad \text{(VII.56)}$$

where C_{ij} — elements in i row of j column, which are already calculated in matrix a_5; a_{ij} — elements in i row of j column of matrix a_4.

By formula (VII.56) there are calculated elements on the leading diagonal and downward from it (steps 2, 4, 6, 8, ...). Elements of each row to the right of the leading diagonal (steps, 1, 3, 5, 7, ...), in contrast to equation (VII.56), are obtained by additional division by the value of diagonal element of this row in determinant a_5 so:

$$C_{ij} = \frac{a_{ij} - (C_{i1}a_{1j} + C_{i2}a_{2j} + C_{i3}a_{3j} + \dots)}{C_{i\,\text{гл. диаг}}}. \qquad \text{(VII.57)}$$

For the considered example the auxiliary determinant according to formula (VII.55) will be

$$|a_s| = \begin{vmatrix} 37{,}5 & 0{,}167 & -0{,}666 & -0{,}212 \\ 6{,}25 & 11{,}46 & -0{,}728 & -0{,}366 \\ 25 & 8{,}33 & 22{,}75 & 0{,}222 \end{vmatrix}$$

In this determinant by the 1st step

$$C_{12} = \frac{6{,}25}{37{,}5} = 0{,}167,$$

$$C_{13} = \frac{-25}{37{,}5} = -0{,}666, \quad C_{14} = \frac{-7{,}92}{37{,}5} = -0{,}212;$$

by the 2nd step

$$C_{22} = 12{,}5 - 6{,}25 \cdot 0{,}167 = 11{,}46,$$

$$C_{32} = 12{,}5 - 25 \cdot 0{,}167 = 8{,}33;$$

by the 3rd step

$$C_{23} = \frac{-12{,}5 + (6{,}25 \cdot 0{,}666)}{11{,}46} = -0{,}728, \text{ etc.}$$

$$C_{34} = \frac{-3{,}28 - (25 - 0{,}212) - (8{,}33 - 0{,}366)}{22{,}75} = 0{,}222.$$

From auxiliary determinant a_s there are found unknowns from x_{m+1} to x_n in the form of a monocolumn matrix:

$$\begin{Vmatrix} x_{m+1} \\ x_{m+2} \\ x_n \end{Vmatrix}$$

The sought unknowns in the form of monocolumn matrix are calculated in the following way.

1. Into calculations there are introduced only elements of auxiliary determinant a_s, located on the right of the leading diagonal.

2. Calculations of monocolumn matrix are produced from bottom to top.

3. Elements are calculated so:

$$\begin{aligned}
&x_n = g_n;\\
&x_{n-1} = g_{n-1} - C_{(n-1)n}\,x_n;\\
&x_{n-2} = g_{n-2} - C_{(n-2)n}\,x_n - C_{(n-2)(n-1)}\,x_{n-1};\\
&x_{n-3} = g_{n-3} - C_{(n-3)n}\,x_n - C_{(n-3)(n-1)}\,x_{n-1} - C_{(n-3)(n-2)}\cdot x_{n-2}.
\end{aligned} \qquad \text{(VII.58)}$$

For the considered example the monocolumn matrix will be

$$\begin{vmatrix} x_3 \\ x_4 \\ x_5 \end{vmatrix} = \begin{vmatrix} -0{,}029 \\ -0{,}205 \\ 0{,}222 \end{vmatrix}.$$

here $x_4 = -0.366 - (-0.728 \cdot 0.222) = -0.205$;
$x_3 = -0.212 - (-0.666 \cdot 0.222) - (0.167)(-0.205) = -0.029$.

After finding unknowns x_3, x_4, and x_5 the earlier excluded unknowns x_1 and x_2 are determined by equation (VII.54):

$$\begin{vmatrix} x_1 \\ x_2 \end{vmatrix} = \begin{vmatrix} 110 & -0{,}916 \\ 200 & 0{,}39 \end{vmatrix} \times \begin{vmatrix} -0{,}029 \\ -0{,}205 \\ 0{,}222 \\ -1 \end{vmatrix}.$$

whence $x_1 = 0.682$; $x_2 = -0.448$.

Now taking into account calculated corrections x_1, x_2, x_3, x_4, and x_5 there can be determined partial pressures of combustion products after the first approximation by formula (VII.36):

$$\begin{aligned}
&\lg p'_{HF} = \lg p^0_{HF} + x_1 = 0{,}8 + 0{,}682 = 1{,}482 \quad p'_{HF} = 30{,}4\ \text{atm};\\
&\lg p'_{H_2} = \lg p^0_{H_2} + x_2 = 0{,}8 - 0{,}448 = 0{,}352 \quad p'_{H_2} = 2{,}245\ \text{atm};\\
&\lg p'_{H} = \lg p^0_{H} + x_3 = 0{,}8 - 0{,}029 = 0{,}771 \quad p'_{H} = 5{,}9\ \text{atm};\\
&\lg p'_{F} = \lg p^0_{F} + x_4 = 0{,}8 - 0{,}205 = 0{,}595 \quad p'_{F} = 3{,}94\ \text{atm};\\
&\lg N'_{\Sigma} = \lg N^0_{\Sigma} + x_5 = 0{,}813 + 0{,}222 = 1{,}035\ N'_{\Sigma} = 10{,}83\ \text{moles};\\
&p'_{\Sigma} = p'_{HF} + p'_{H_2} + p'_{H} + p'_{F} = 53{,}32\ \text{atm}.
\end{aligned}$$

This finishes calculation with introduction of corrections after the first approximation. Calculations of subsequent approximations are carried out analogously, namely during each subsequent approximation instead of initial values p^0_{HF}, $p^0_{H_2}$, p^0_H, p^0_F and N^0_x into calculation formulas there are introduced the values of these unknowns, found with corrections from preceding approximation.

§ 12. Calculation of Theoretical Temperature and Equilibrium Composition of Combustion Products at Rated Constant Pressure in the Chamber

With such boundary conditions the system of equations for determining the composition of products (VII.32-VII.35) should be augmented by one more equation for finding the combustion temperature. Such an equation can be formulated on the basis of the law of conservation of energy in the form of enthalpy balance. At constant pressure there should be observed equality dI = 0.

In integral form this equality is written so:

$$N_x I_T^{T_0} \pm \Delta I = I_\Sigma^T = \sum N_i I_i^T. \qquad \text{(VII.59)}$$

where $N_x I_T^{T_0}$ — enthalpy of liquid-propellant at its combustion chamber feed temperature; $\pm\Delta I$ — heat loss during combustion or heat addition from an external source; I_Σ^T — enthalpy of combustion products at combustion temperature T.

With adiabatic insulation of the combustion chamber from the environment, absence of losses (because of poor carburetion and physical incompletness of combustion) and absence of external heat source instead of (VII.59) the equation of enthalpy balance will be in such a form

$$N_x I_T^{T_0} = \sum N_i I_i^T. \qquad \text{(VII.60)}$$

Let us linearize this equation by Taylor expansion with respect to increases of $\Delta \lg T$ and $\Delta \lg N_x$ in the vicinity of initial approximation $(p_i^0, N_x^0, T^0, \ldots)$. Then we obtain

$$N_x^0 I_T^{0} + I_T^{0} \left(\frac{\partial N_x}{\partial \lg N_x}\right)_0 \Delta \lg N_x = \sum N_i^0 I_i^{T^0} +$$
$$+ \sum I_i^{T^0} \left(\frac{\partial N_i}{\partial \lg N_i}\right)_0 \Delta \lg N_i + \sum \Lambda_i^0 \left(\frac{\partial I_i}{\partial \lg T}\right)_0 \Delta \lg T.$$

Considering that

$$\left(\frac{\partial N}{\partial \lg N}\right)_0 = N^0 \ \text{и} \ \left(\frac{\partial I_i}{\partial \lg T}\right)_0 = \left(\frac{\partial I}{\partial T} \frac{\partial T}{\partial \lg T}\right)_0 = (c_{p_i} T)_0,$$

let us write equation of enthalpy balance (VII.60) in the final form:

$$\sum N_i^0 I_i^{T^0} \Delta \lg N_i + (c_p T)_0 \Delta \lg T - N_x^0 I_T^{0} \Delta \lg N_x = -\delta_I \,, \qquad \text{(VII.61)}$$

where

$$(c_p T)_0 = T^0 \sum (c_{p_i} N_i)_{T=T^0} \ \text{и} \ \delta_I = \sum (N_i^0 I_i^{T^0}) - (N_x^0 I_T^{0}).$$

Equation (VII.61) is suitable during calculation of any components of combustion products. When performing calculations for N_x moles of propellant for gaseous components, instead of N_i we put partial pressures $p_i = N_i$ in equation (VII.61), and for condensed substances we keep N_i.

With application of general method of solution of totality of equations by means of successive approximations, instead of equations (VII.32-VII.35) there are used linear equations (VII.45-VII.48).

Let us write the entire system of equations for calculation of temperature and composition of combustion products (neglecting possible ionization), in the sequence they are written in the initial matrix of coefficients for solution:

1. Equations (VII.47a) for equilibrium during dissociation of gases

$$\Delta\lg p_i - a_i\Delta\lg p_A - b_i\Delta\lg p_B - c_i\Delta\lg p_C - \ldots - L_{K_i}\Delta\lg T = -\delta_i .$$

2. Balanced equations of elements (VII.45):
for atoms A

$$\sum a_i N_i^0 \Delta\lg N_i - L_A \Delta\lg N_x = -\delta_A L_A ;$$

for atoms B

$$\sum b_i N_i^0 \Delta\lg N_i - L_B \Delta\lg N_x = -\delta_B L_B ;$$

. . . .

3. Equations (VII.47b) for equilibrium during dissociation with the presence of condensed phase

$$-a_i\Delta\lg p_A - b_i\Delta\lg p_B - c_i\Delta\lg p_C - \ldots - L_{K_i'}\Delta\lg T = -\delta_{ik} .$$

4. Equations (VII.48a) of total number of moles of combustion products:
for all substances

$$\sum N_i \Delta\lg N_i = -\delta_N N_\Sigma^0 ;$$

for only gaseous substances

$$\sum p_i \Delta\lg p_i = -\delta_p p_\Sigma^0 .$$

5. Equations (VII.61) for enthalpy balance

$$\sum N_i^0 I_i^{T\bullet} \Delta\lg N_i + (c_p T)_0 \Delta\lg T - N_x^0 I_T^{t\bullet} \Delta\lg N_x = -\delta_I .$$

where

$$(c_pT)_0 = T^0\sum(c_{p_i}N_i)_{T-T^0} \text{ и } \delta_I = \sum(N_iI_i)_{T-T^0} - (N_z^0 I_T^0) .$$

§ 13. Calculation of Theoretical Temperature and Equilibrium Composition of Combustion Products in the Nozzle Box with Isentropic Flow

The usual theoretical scheme for such calculations is the assumption concerning isentropic character of processes, occuring in the nozzle box.

As boundary condition for calculation there is assigned pressure in the examined nozzle section, including the nozzle exit. Typical calculations are produced for the nozzle exit section, since by results of such calculations there is directly calculated the theoretical specific engine thrust.

For determination of unknowns, characterizing the composition of combustion products in the nozzle box, previously there was used the system of equations (VII.45-VII.48), examined above in detail.

For determination of temperature this system is supplemented by one more equation, expressing the constancy of entropy during flow in nozzle box dS = 0.

In integral form this equality is written:

$$S_{\text{к}} = S_a, \qquad \text{(VII.62)}$$

where $S_{\text{к}}$ – entropy of combustion products ahead of the nozzle box in the combustion chamber, determined by results of calculation of combustion products in the chamber; S_a – entropy of combustion products in the examined nozzle section (at specific composition, temperature T_a and pressure p_a in this section).

Entropy of combustion products is determined on the basis of tabular values of standard absolute entropy of substances, designated by S_i^0. By standard value of entropy there is conditionally implied the value of entropy for assigned temperature at atmospheric pressure.

Under combustion chamber and nozzle box conditions the pressure can differ from atmospheric. Let us consider the formula for calculation of gas entropy at any pressure.

According to the first law of thermodynamics

$$TdS = c_p dT - v dp.$$

At the same temperature (dT = 0) from change of pressure the entropy is changed so:

$$dS = -\frac{v dp}{T}.$$

Replacing $\frac{v}{T} = \frac{R}{p}$ by equation of state and integrating by pressure, from the preceding equality we will obtain

$$S_i = S_i^0 - R_\mu \ln p, \tag{VII.63}$$

where R_μ = 1.987 cal/mole·deg; p — atm.

Value of entropy of combustion products is determined by summation of entropy of all the substance components

$$S_z = \sum S_i N_i. \tag{VII.64}$$

Considering condition (VII.29), $N_i = p_i$ for gases. For condensed substances as S_i there is taken the standard value of entropy S_i^0. Equation (VII.64) gives total value of entropy of combustion products. Specific entropy, related to one mole of propellant, from which these combustion products are obtained, will be

in the combustion chamber

$$S_{\text{к}}=\frac{(S_{\Sigma})_{\text{к}}}{N_{x\text{к}}}=\frac{\Sigma(S_iN_i)_{\text{к}}}{N_{x\text{к}}}, \qquad \text{(VII.65)}$$

where $N_{x\text{к}}$ — number of moles of propellant, for which the composition of combustion products in the chamber was calculated;

in nozzle box

$$S_{\text{а}}=\frac{(S_{\Sigma})_{\text{а}}}{N_{x\text{а}}}=\frac{\Sigma(S_iN_i)_{\text{а}}}{N_{x\text{а}}}, \qquad \text{(VII.66)}$$

where $N_{x\text{а}}$ — number of moles of propellant, for which the composition of combustion products in the nozzle is calculated.

Equation (VII.62) for conservation of entropy during expansion in the nozzle taking into account (VII.64-VII.66) will be (index a is dropped)

$$\frac{\Sigma S_iN_i}{N_x}-S_{\text{к}}=0. \qquad \text{(VII.67)}$$

Let us rewrite this equation in logarithmic form:

$$\lg\sum S_iN_i-\lg N_x-\lg S_{\text{к}}=0.$$

After Taylor expansion by increases of $\Delta\lg N_i$ or $\Delta\lg p_i$ for gases $\Delta\lg N_x$ and $\Delta\lg T_{\text{а}}$ in the vicinity of initial approximate value of unknowns N_i^0; N_x^0; $T_{\text{а}}^0$ and linearization we will obtain

$$\lg\sum(S_iN_i)^0+\frac{1}{\Sigma(S_iN_i)^0}\sum\left[S_i+\frac{\partial S_i}{\partial\lg N_i}\right]^0\times$$

$$\times N_i^0\Delta\lg N_i+\frac{1}{\Sigma(S_iN_i)^0}\sum\left(N_i\frac{\partial S_i}{\partial\lg T}\right)^0\Delta\lg T_{\text{а}}-$$

$$-\lg N_x^0-\Delta\lg N_x-\lg S_{\text{к}}=0.$$

After further conversions taking into account $\frac{\partial S_i}{\partial \lg T} = c_{p_i}$ it is possible to write

$$\sum \left[S_i + \frac{\partial S_i}{\partial \lg N_i} \right]^0 N_i^0 \Delta \lg N_i - \sum (S_i N_i)^0 \Delta \lg N_x + \\ + \sum (c_{p_i} N_i)^0 \Delta \lg T_a = - [\lg \sum (S_i N_i)^0 - \lg N_x^0 - \\ - \lg S_k] \sum (S_i N_i)^0 .$$

Let us designate

$$S' = S_i^0 + \frac{\partial S_i}{\partial \lg N_i}; \qquad \text{(VII,68)}$$

for gases

$$S' = S_i^0 - 1{,}987 (\ln p_i); \qquad \text{(VII.69)}$$

for condensed substances $S' = S_i^0$.

Let us write equation of conservation of entropy in final linear form

$$\sum (S_i' N_i)^0 \Delta \lg N_i - (S_z)^0 \Delta \lg N_x + c_p^0 \Delta \lg T_a = -\delta_S (S_z)^0, \qquad \text{(VII.70)}$$

where

$$(S_z)^0 = \sum (S_i N_i)^0; \\ \delta_S = [\lg (S_z)^0 - \lg N_x^0 - \lg S_k]; \\ c_p^0 = \sum (c_{p_i} N_i)^0 .$$

Here superscript 0 indicates that these values are calculated according to initial (preceding) approximation.

Taking into account (VII.63-VII.69), formula (VII.70) is valid for all components of the heterogeneous mixture of combustion products.

For gaseous substances instead of N_i there are substituted values of partial pressures $p_i = N_i$.

System of equations (VII.45-VII.48) together with equation (VII.70) for calculation of theoretical temperature and composition of combustion products in the nozzle is solved by the general method of successive approximations, described above.

For calculation of isentropic outflow at chemical and energy equilibrium the pressure in the considered section or at nozzle section p_a is assigned. Furthermore, from results of calculation of combustion in the chamber pressure p_K, temperature T_K and composition of combustion products before the nozzle are assumed known.

In order to tentatively assign the expected gas temperature in the nozzle for the first approximation T_a^0, it is possible to use the mean value of index of expansion process:

for propellants such as oxygen + kerosene n = 1.12-1.15;
for propellants such as HNO_3 + kerosene n = 1.17-1.2.

Then by approximate equation it is possible to take

$$T_a^0 \approx T_K\left(\frac{p_a}{p_K}\right)^{\frac{n-1}{n}}. \qquad \text{(VII.71)}$$

Thus, the composition of combustion products in the nozzle for the very first (initial) approximation can be estimated by composition of combustion products in the chamber

$$p_i^0 \approx p_{iK}\left(\frac{p_a}{p_K}\right). \qquad \text{(VII.72)}$$

A distinct feature of calculations for the nozzle exit section is considerably lower gas temperature than in the combustion chamber. Therefore, in a number of cases the unknowns, relating to content of atomic gases from calculation, can be excluded, and thus, the system of calculation equations is considerably simplified.

Calculation of isentropic expansion with determination of composition of combustion products is usually produced for the nozzle exit section and is finished by determination of the following values:

1) composition of combustion products, prescribed by partial pressures or molar content, and gas temperature;

2) average molecular weight of combustion products or gas constant:

$$\mu_a = \frac{\Sigma \mu_i N_i}{N_к} = \frac{\Sigma \mu_i p_i}{p_к};$$

$$R_a = \frac{1.987}{\mu_a} \frac{\text{kcal}}{\text{kg}^\circ\text{C}} = \frac{848}{\mu_a} \frac{\text{kg}\cdot\text{m}}{\text{kg}^\circ\text{C}};$$

3) average isentropic index $n_{из}$ during gas flow from the combustion chamber to nozzle exit, which we will subsequently designate through k:

$$k = n_{из} = \frac{\lg p_к/p_a}{\lg \frac{p_к}{p_a} \cdot \frac{R_a T_a}{R_к T_к}}.$$

Sometimes this formula for k is writen more approximately, neglecting the difference of R_a and $R_к$, which leads to divergences in the determination of average index of the expansion process;

4) theoretical exit velocity. It is more correct to calculate exit velocity at isentropic process of expansion by equation of conservation of energy in the form of enthalpy balance

$$I_к = I_a + \frac{AW_a^2}{2g}. \qquad \text{(VII.73)}$$

whence theoretical velocity

$$W_{ат} = \sqrt{\frac{2g}{A}(I_к - I_a)} = 91{,}53\sqrt{I_к - I_a}. \qquad \text{(VII.75)}$$

In this formula the enthalpy of combustion products in the chamber $I_к$ and enthalpy in the nozzle exit section I_a are expressed in specific dimensionality, relating to one kilogram, and are calculated by equations

$$I_к = \frac{1}{\mu_к p_к}\Sigma(I_i p_i)_к;$$
$$I_a = \frac{1}{\mu_a p_a}\Sigma(I_i p_i)_a. \qquad \text{(VII.76)}$$

where I_i – enthalpy relating to one mole.

Frequently for calculation of theoretical exit velocity there is used approximate formula

$$W_{ат} \simeq \sqrt{2g\frac{k}{k-1}RT_к\left[1-\left(\frac{p_a}{p_к}\right)^{\frac{k-1}{k}}\right]}. \qquad \text{(VII.77)}$$

In this formula, besides the mean value of k, there is also introduced the mean value of gas constant R, variable from $R_к$ in the combustion chamber to R_a at nozzle exit;

5) theoretical specific thrust at calculated conditions

$$P_{уд.т} = \frac{W_a}{g} = 9{,}33\sqrt{I_к - I_a}. \qquad \text{(VII.78)}$$

After finding the average index of isentropic process of expansion k (pertaining to entire length of the nozzle), it is possible to approximationly determine the gas flow parameters in the nozzle throat, where number M = 1.

By average isentropic index k there are found pressure in the throat

$$p_{\text{кр}} = p_{\text{к}}\left(\frac{2}{k+1}\right)^{\frac{k}{k-1}}.$$

product of $R_{\text{кр}}\,T_{\text{кр}}$ in this section

$$R_{\text{кр}}T_{\text{кр}} = R_{\text{к}}T_{\text{к}}\left(\frac{2}{k+1}\right).$$

velocity in throat

$$W_{\text{кр}} = \sqrt{kgR_{\text{кр}}T_{\text{кр}}} = \sqrt{2g\frac{k}{k+1}R_{\text{к}}T_{\text{к}}}.$$

Determination of these values is used for theoretical calculation of specific throat

$$f_{\text{кр}_{\text{т}}} = \frac{F_{\text{кр}}}{G} = \frac{\sqrt{R_{\text{к}}T_{\text{к}}}}{p_{\text{к}}\left(\frac{2}{k+1}\right)^{\frac{k+1}{2(k-1)}}\sqrt{kg}} \qquad \text{(VII.79)}$$

and specific impulse of pressure in the combustion chamber, called complex[1]

$$\beta = \frac{p_{\text{к}}F_{\text{кр}}}{G} = p_{\text{к}}f_{\text{кр}} = \frac{\sqrt{R_{\text{к}}T_{\text{к}}}}{\left(\frac{2}{k+1}\right)^{\frac{k+1}{2(k-1)}}\sqrt{kg}}. \qquad \text{(VII.80)}$$

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[1] In foreign literature instead of complex β there is used a value, called characteristic velocity c*, which is connected with complex β so: c* = βg m/s.

Product of $p_{\text{к}}F_{\text{кр}}$ is a component of total engine thrust, developed thanks to gas pressure on the nonbalanced part of the front wall of the combustion chamber, with area equal to $F_{\text{кр}}$.

Complex β has dimensionality kg·s/kg and is the basic component of specific thrust.

Value of specific throat area is connected with complex β and pressure in the combustion chamber $p_{\text{к}}$. The greater the pressure in the combustion chamber, the less is $f_{\text{кр}}$.

Value of complex β according to formula (VII.80) depends on the product of $R_{\text{к}}T_{\text{к}}$ and the mean value of isentropic index k. These two values are affected by:

a) type of propellant and the ratio of fuel and oxidizer α, determining the composition of combustion products, on which $R_{\text{к}}T_{\text{к}}$ and k depend;

b) pressure in combustion chamber $p_{\text{к}}$, lowering the degree of dissociation of combustion products, from which $R_{\text{к}}T_{\text{к}}$ and k are changed;

c) gas expansion ratio in the nozzle box, from which is changed the value of average k, calculated for entire length of nozzle. Thus, because of the application of average k, the value of complex β turns out to be dependent on the supersonic part of the nozzle. The higher the nozzle expansion ratio, the greater this influence is.

If we eliminate inaccuracies in determining the theoretical value of complex β by introduction to calculation of the mean value of k not for the entire nozzle, but only for the subsonic part, then this complex will be determined entirely by intrachamber parameters: propellant used and pressure in the combustion chamber.

Complex β is easily determined during engine tests by measurement of pressure in the chamber and consumptions of propellant components.

This permits comparing the experimental value of $\beta_{\text{эксп}}$ with theoretical, calculated by formula (VII.80).

On the basis of such a comparison it is possible to check the correctness of the method of calculation of temperature and composition of combustion products, and it is possible to judge the degree of perfection of intrachamber processes with regard to propellant combustion.

Therefore, for detailed analysis, in order to eliminate the influence of the supersonic part of the nozzle on theoretical determination of β, it is expedient to perform additional calculation of temperature and composition of combustion products in the throat itself. After completing such calculation one can determine more precise theoretical values of the required throat area and the value of complex β.