TRANSLATION

INTRODUCTION TO ROCKET TECHNIQUE
(VVEDENIYE V RAKETNUYU TEKHNIKU)

By V. I. Feodos'yev, G. B. Sinyarev

PREPARED BY
LIAISON OFFICE
TECHNICAL INFORMATION CENTER
MCLTD
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

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Newest rocket terminology was used throughout, based on recent publications, advance notices of papers read before the Radiation Conference in Vermont, etc.

The term rocket propellant was used whenever specific discussion of its components was involved. The components, in that case, were called combustible and oxidizer, while the term fuel was reserved for general descriptions of rocket fuels.

The term "Teplovospriimchivost'" was rendered as "heat absorptivity" in agreement with the symbol Q used. The term "teploemkost'" was rendered as heat capacity in agreement with the symbol c used. Although heat absorptivity is not too common a term, Q is the international symbols for heat absorbed while (−Q) is the symbol for heat given off. "Susceptibility" would not be as good and heat capacity would be wrong.

The terms "calorific value", "heat value", and "heating value" were used intermixedly, as fitted best into the context. All mean the same and are expressed in thermal units per pound (or kg).

The terms "vesovaya i obemuaya teplotvornyye" were rendered as heat value per unit weight and unit volume, in agreement with standard practice, and then shortened to "weight heat value" and "volume heat value", respectively, as in the foreign text.

In writing nuclear reactions, the more modern arrangement of using the subscript for the atomic number in front of the symbol was used (thus, $_{92}U^{235}$ not U^{235}_{92}).

The term "shashka" was rendered as powder grain, despite the fact that it is wrong from a physics viewpoint. However, the term has become standard terminology in rocket technique for any size powder charge used in a rocket. Thus, tubular grain, cruciform grain, etc was used in translation.

The Translator

Table of Contents

CHAPTER IV

FUELS OF ROCKET ENGINES

1. The Chemical Energy of Rocket-Engine Fuels

Sources of Energy for Rocket Engines

A rocket engine, like any other engine, needs some source of energy for its operation.

The only source of energy used in rocket engines today is chemical energy. When an engine operates, this energy may be liberated in reactions of two types. The most widely used is the reaction of combustion. This reaction is utilized in the operating processes in the overwhelming majority of existing thermal engines. The reactions of decomposition of certain substances are also used for the liberation of chemical energy, provided this process of decomposition is accompanied by the liberation of heat. In rocket engines, for example, the reaction of the decomposition of hydrogen peroxide is widely used.

A rocket engine requires not only a source of energy, but also a reserve of mass, which is ejected by the engine during the course of its operation. The substance ejected from a rocket is usually termed the working body.

In existing engines, the source of chemical energy is the fuel, while the working body is constituted by the reaction products of combustion or decomposition of the fuel. Thus the fuel is at first the carrier of chemical energy, and then of kinetic energy.
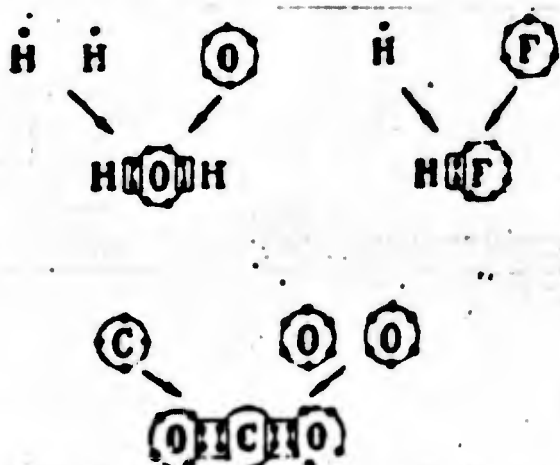
1

Nuclear energy is a promising source of energy for rocket engines. It is not used in rocket engines today, but without doubt will be used in the near future. Nuclear fuel will evidently be used only as a source of energy, while the working body will have to be carried additionally on board of the rocket.

The Process of Combustion and Chemical Energy

By process of combustion we mean the chemical process between two substances, a combustible and an oxidizer, which is accompanied by the liberation of a large amount of heat.

Let us consider the simplest process of combustion, the reaction of combustion of a combustible and oxidizer elements taken in the pure, atomic form.

The energy level of atoms is determined by the structure of the outer electron shell of the atom. A completely definite number of electrons is found in the outer shell of the atom when it is completely filled. For the elements ordinarily used in rocket-engine fuels, this number is eight. Hydrogen is an exception, having a maximum of two electrons in its outer shell.

The filling of the outer shell by electrons is accompanied by a fall in the energy level of the atom. The atom is at its minimum energy level when the outer shell is completely filled with electrons.

Fig.4.1 - Diagram of the Course of Chemical Reactions. The dots indicate electrons. The electrons enclosed in a box belong simultaneously to two atoms shell is completely filled with electrons.

If we consider the structure of atoms of combustible and oxidizer elements, we will find that their outer shells are incompletely filled with electrons. Thus (Fig.4.1) one electron (out of two) is missing in the hydrogen atom, four electrons

are missing in the carbon atom, two in the oxygen atom, and one electron (out of eight) in the fluorine atom.

No change in the atomic structure takes place during the chemical reaction of combustion, since the total number of electrons in the atoms of the combustible and oxidizer elements remains the same. On formation of the combustion product, however, the electron shells of the reacting atoms are interwoven and transformed so that some electrons are simultaneously in the shells of atoms of the combustible and oxidizer elements. For example, on combustion of hydrogen with oxygen to form water vapor, the electron shells are so transformed that, as a result, two groups of two electrons each will be located simultaneously in the shell of an oxygen atom and in that of a hydrogen atom. In this case the oxygen atom in the water molecule has eight electrons in its outer shell, while the hydrogen atoms have two electrons each, i.e., the shells of all the atoms are completely filled with electrons.

In exactly the same way, in the hydrogen fluoride molecule (cf.Fig.4.1) the sharing of electrons results in the complete filling, with electrons, of the shells of all atoms in the combustion product. For this reason, the energy level of the molecule of the combustion product is considerably lower than the energy level of the atoms before they entered into combination. It is the difference between these energy levels that determines the quantity of chemical energy liberated during combustion.

Since the energy levels of the original substances and of the products of combustion reaction depend on the structure of the respective particles, it follows that the quantity of chemical energy liberated during combustion is always constant and is entirely independent of all external conditions, such as pressure, temperature, volume, etc.

This is the manner in which the process of combustion of atomic substances takes place. In reality, however, the combustible and oxidizer elements in liquid-fuel rocket engines are not in the atomic state but enter into the composition of

molecules of elementary substances or, most often, of compounds.

In this case, the combustion process with respect to the energy yield, may be imagined as proceeding in the following manner: A substance in the molecular form is decomposed into atoms of the corresponding elements, with the consumption or liberation of chemical energy. The atoms then combine into combustion products, always with liberation of chemical energy. The total effect with respect to the yield of chemical energy is determined by the algebraic sum of the chemical energies corresponding to each of these component process.

It should be noted that the liberation of chemical energy during the combustion process requires an initial activation energy. This energy is used up in bringing the reacting atoms into the state in which their chemical interaction can begin. For example, hydrogen and oxygen or carbon monoxide and oxygen can remain for an indefinite time in the state of mixture. Chemical reaction in such mixtures begins only after ignition. It is this process of ignition that supplies the necessary energy of activation to the mixture ready for combustion. If combustion has been initiated in any group of particles of the mixture, then the energy of activation for the other particles is drawn from the chemical energy of the neighboring reacted particles, thus causing the combustion to spread.

The value of the activation energy varies for different mixtures. The higher the activation energy, the more difficult will it be to ignite the mixture.

Chemical Energy and Heat of Formation

The chemical energy liberated in combustion reactions may be determined in two ways.

The first method is to calculate from the spectra of particles (atoms and molecules) the energy levels of these particles before and after reaction, and to find the quantity of chemical energy corresponding to a given transformation of matter, from their difference.

The second method consists in a calorimetric determination of the heats of formation (which are also called heats of combustion) of the substance. In this case, the necessary reaction is run in a special vessel (a calorimeter), as a result of which the chemical energy is transformed into thermal energy. This energy is consumed in heating the reaction products. After completion of the combustion process, the reaction products are cooled to the temperature of the original products before beginning of the reaction, and the quantity of heat removed from the reaction products is measured. The quantity of heat determined in this manner is called the heat of formation of the substance, as distinguished from the chemical energy found by the first method.

The heat of formation has a definite relation to the chemical energy, although it is not equal to it. The difference between the heat of formation and the chemical energy is that, during combustion and the corresponding changes of the substance, there is also a change in the heat capacity of the original substance.

This change in the heat content or enthalpy is as follows:

$$\Delta Q = \int_0^T c_{prod}\, dT - \int_0^T c_{orig}\, dT. \tag{4.1}$$

where c_{prod} is the heat capacity of the reaction product;

c_{orig} is the heat capacity of the original substances.

If the heat capacities are independent of the temperature, then

$$\Delta Q = (c_{prod} - c_{orig})\, T. \tag{4.2}$$

In combustion reactions, the heat capacity of the reaction products is not equal to the heat capacity of the original substances, since substances of properties different from those of the original substances are formed during combustion.

Moreover, the heat capacity of gaseous substances also depends on the conditions under which the reaction takes place (at constant pressure or at constant volume). For this reason, the change in the quantity of energy contained in the substances before and after reaction depends on the conditions under which this reaction takes

place, i.e., on the pressure, volume, and initial temperature.

The temperature T has the greatest influence on the value of ΔQ.

The heat of formation used in liquid rocket engine calculations is usually related to the following conditions: constant pressure of one absolute atmosphere, at room temperature. In this case, the heat of formation is considered the change in the value of the heat content H of the combustion products and is denoted by ΔH_T^0. The superscript indicates the pressure at which the heat of formation is determined, and the subscript denotes the absolute temperature. If the heat of formation is determined at the absolute pressure $p = 1$ kg/cm^2, then the superscript is written as "0".

Knowing the heat of formation and the heat capacity of the substances participating in the reaction, it is always be possible to calculate the chemical energy as the algebraic difference:

$$\Delta H_T^0 \pm \Delta Q.$$

Since, at $T = 0$, we have $\Delta Q = 0$, the chemical energy may be defined as the heat of formation at absolute zero and denoted by ΔH_0^0. This quantity serves as a measure of the chemical energy and is widely used in many thermodynamic calculations.

In view of the fact that the heat of formation of the combustion products depends on the external conditions, so-called standard conditions are used in determining it. For the most part, the heats of formation of substances are determined at a temperature of 18°C, 20°C, or 25°C (291.16, 293.16 or 298.16°C abs). In this case, the difference between the chemical energy and the heat of formation of the corresponding products is relatively small.

Since the heat of formation of a substance depends on the form (atomic, or elementary substances or compounds) in which the elements composing the given substance are taken, the heat of formation is always related not only to the standard conditions, but also to standard states of the elements. The standard state means the state of an element in the form in which it is most widely distributed in nature. Thus the following standard states are adopted for the combustible and

oxidizer elements in most common use: for hydrogen, oxygen, and nitrogen, that of the molecular gases H_2, O_2, N_2; for carbon, β-graphite; for a metal, the crystalline form in which it is most often met in nature. The sign of the heat of formation is determined by the fact that the loss of energy of the system entering into the reaction is, naturally, considered negative. For this reason, the heat of formation of combustion products always has a negative sign.

The Calorific Value of a Fuel

By the calorific or heat value we mean the quantity of heat liberated on combustion of unit weight of the fuel. We will denote this value by K_G. It has the dimension kcal/kg.

The heat value of a fuel is equal to the heat of formation of the products of the combustion reaction, taken with reversed sign, since the chemical energy of the substance lost on formation of the combustion products is, according to the law of conservation of energy, completely converted into heat. Thus,

$$K_G = -\Delta H_T^0$$

The value of the heat of formation is usually given in kcal/gm-mole and is easily converted into the quantity of heat per unit weight, by using the relation

$$\Delta H \text{ kcal/kg} = \frac{1000}{\mu} \Delta H \text{ kcal/gm-mole}$$

where μ is the molecular weight of the products of the combustion reaction.

Attention should be paid to the fact that in a rocket, both the combustible and the oxidizer are carried on board, and consequently are of the same value. For this reason, we will always relate the calorific value or the heat of formation to the total mass of the substances consumed during the reaction rather than to the weight of the combustible alone, as is done in ordinary thermal engineering, where the consumption of oxidizer, which is atmospheric air, is never taken into account since the oxygen is taken from the ambient atmosphere.

The combustible and oxidizer components used in rocket propellants should naturally be those having the maximum amount of chemical energy. In this case, a larger supply of energy may be placed in a rocket of given dimensions. Since there are a limited number of chemical elements that exist in nature, it is natural to select from them those having the greatest supply of chemical energy.

As far back as the time of K.E.Tsiolkovskiy, it was pointed out in one of his first works "The Rocket in Cosmic Space" that a definite law for the values of the chemical energy of the elements must exist, in connection with the Mendeleyev periodic system. In fact, the heats of formation of the combustion products of the various elements fall into a regular arrangement, forming periods corresponding to the rows of elements in the Mendeleyev Periodic Table. More detailed investigations of this question led to the following results:

Of all the elements, only two, oxygen and fluorine, can be used as oxidizer elements, yielding a large supply of chemical energy and ensuring the necessary intensity of the combustion reaction. The other oxidizer elements, such as chlorine, bromine, and iodine, do not yield great chemical energies. As combustibles, the following elements yield the greatest effect: beryllium, lithium, boron, aluminum, magnesium, silicon, hydrogen, and carbon.

Before discussing in greater detail the properties and energetic characteristics of the various elements, let us refine the basic indices by which the components of liquid-fuel rocket engine propellants, the combustible and oxidizer, must be evaluated.

Basic Requirements to be Met by Rocket Propellants

In evaluating various substances for use as rocket fuels, the fundamental requirements that liquid-fuel rocket engine propellants must meet are used as basis. These basic requirements are as follows:

1. High weight concentration of chemical energy, which is determined by the

heat value of the fuel. The greater the value of K_G the greater will be the kinetic energy that can be imparted to the combustion product, and the higher will be the exhaust velocity and the specific thrust of the engine.

2. Greatest possible energy reserve per unit volume occupied by the fuel, i.e., the greatest possible heat value per unit volume of the fuel (this same quantity is sometimes called the heat density). The greater this value, the less volume will be occupied by the necessary fuel supply, the less will be the relative weight of the rocket structure, and the smaller will be the value to which μ_K for the rocket can be reduced.

The bulk heat value is

$$K_V = \gamma_f K_0,$$

(4.3)

where γ_f is the specific gravity of the fuel in kg/ltr.

The specific gravity of a propellant consisting of a combustible and an oxidizer is, in turn, determined by the formula

$$\gamma_f = \frac{1+\nu}{\dfrac{1}{\gamma_c} + \dfrac{\nu}{\gamma_0}},$$

(4.4)

where γ_c is the specific gravity of the combustible;

γ_0 is the specific gravity of the oxidizer;

ν is the quantity of oxidizer in kg, per kilogram of combustible.

We note that

$$\nu = a \, \nu_0,$$

where ν_0 is the quantity of oxidizer theoretically required, which is determined

from the ordinary material (weight) balance of chemical reactions under the

condition of their completion at minimum consumption of oxidizer;

a is the coefficient of loss of oxidizer; for liquid-fuel rocket engines, the

coefficient a is usually somewhat less than unity.

3. A high heat capacity per unit weight of the combustion product and a cor-

respondingly low combustion temperature. Since the process of combustion in a liquid rocket engine proceeds under constant pressure, the combustion temperature, in first approximation, is determined by the relation

$$T = \frac{K_0}{c_p},$$ (4.5)

where c_p is the weight heat capacity of the combustion products under constant pressure. For this reason, at the same heat value of the fuel, the temperature in the combustion chamber will be lower, the greater the heat capacity of the combustion products.

A decrease in the combustion temperature of a fuel is of substantial importance for the design of engines that will operate reliably on this fuel. Moreover, a decrease in the combustion temperature decreases the degree of dissociation of the combustion products (cf. later in text) and increases the efficiency of the engine.

For gases with the same number of atoms in the molecules, the heat capacity c_{pm}, expressed in kcal/g-mole deg, varies within narrow limits. Since 1 kg contains 1000μ gram-moles of combustion products (where μ is their molecular weight), the heat capacity per unit weight will be:

$$c_p = c_{pm} \frac{1000}{\mu} \text{ kcal/kg deg}$$ (4.6)

Consequently, the lower the molecular weight of the combustion products, the higher will be their weight heat capacity and the easier will it be to use this fuel in an engine.

The molecular weight of the combustion products may also be characterized by two other quantities, namely the gas constant of the combustion products R and the so-called quantity of gas formation v.

It is well known that for any gas, the universal gas constant is $\bar{R} = 0.848$ kg gm/gm-mole deg or, expressed in thermal units,

$$\Delta R = \frac{0.848}{427} = 1.986 \times 10^{-3} \text{ kcal/gm-mole deg}$$

The weight gas constant

$$R = \frac{848}{\mu} \text{ kgm/kg deg}$$

The lower the molecular weight of the combustion products, the greater will be their gas constant. Thus the value of the gas constant for the combustion products of rocket fuels should be as great as possible.

We will later have occasion to use the equation of state, written for 1 kg of gas:

$$pv = RT$$

or

$$v = R \frac{T}{p}$$

As we see, under given conditions, the volume of the combustion products v formed is proportional to the value of the gas constant R. The volume of the combustion products under normal conditions ($T = 291.16^\circ$ abs; $p = 1$ kg/cm^2) is known as the gas formation. It shows how many liters of combustion products are formed from 1 kg of fuel under normal conditions. The greater this quantity, the greater will be the gas constant of the combustion products, and the smaller their molecular weight. Consequently, the gas formation in the combustion of the fuel should be the maximum possible.

4. The physical state of the combustion products is very important for the process of expansion and of transformation of thermal energy into kinetic energy.

The conversion of thermal energy into the kinetic energy of directed motion takes place most simply in the case where the combustion products are gaseous. For solid products, expansion is impossible, so that solid products must give up their

thermal energy to the gas by means of thermal conduction or radiation. Only the heat of the solid product which is given up in this way to the gas participates in the process of expansion and will be utilized to form the kinetic energy of the jet.

It is obvious that the presence of solid particles in the nozzles is undesirable. Consequently the boiling point of the combustion products must be sufficiently low. In addition, in order not to lose, by evaporation, a large part of the heat liberated during combustion, the heat of vaporization of the combustion products must be as small as possible.

Analysis of Combustible and Oxidizer Elements as Components of Rocket Propellants

Table IV.1 gives the principal properties and energetic characteristics of the combustible and oxidizer elements of liquid rocket engine propellants.

In studying this Table, the empty columns and doubtful data (numbers in parentheses) that it contains may seem surprising. Although most of the substances enumerated in the Table have long been used in technology, a thorough study of their properties and of the properties of their compounds has been taken up only in recent years, in connection with the demands of rocket engineering. The literature data on these substances are exceedingly contradictory and are often changed. The information in the Table, however, is sufficient to give a basic evaluation of these elements as components of liquid rocket engine propellants.

Among the oxygen compounds of the elements, beryllium oxide has the greatest heat of formation per unit weight BeO, 5830 kcal/kg. This value considerably exceeds the heat values of the hydrocarbon fuels used today. Boron oxide, B_2O_3, and lithium oxide Li_2O, also have a high heat of formation. The heat of formation is lower for water H_2O than for magnesium oxide MgO, aluminum oxide Al_2O_3, and silicon oxide SiO_2. Carbon dioxide CO_2 has the lowest heat of formation.

The volume heat of formation is greatest for beryllium oxide and smallest for water. The latter circumstance constitutes a substantial shortcoming of liquid

Name of Element	Symbol or Formula	Phase	Molecular Weight	$\Delta H^0 298.16$ kcal/gm-mole	Oxygen Combustion Products					
					K_G kcal/kg	V_o kg/kg	γ kg/ltr	K_V kcal/ltr	t_{bp} °C	ΔH_{evap} kcal/kg
Hydrogen	H_2O	gas	18.016	—57.798	3210	7.95	0.42	1350	100	—
Lithium	Li_2O	solid	29.88	—142.400	4760	1.15	0.75	3570	1300	(1160)
Beryllium	BeO	solid	25.01	—146.000	5830	1.78	1.52	8850	(3500)	very high
Boron	B_2O_3	solid	69.64	—302.000	4350	2.21	1.28	5570	—	—
Carbon	CO_2	gas	44.01	—94.052	2140	2.66	1.32	2830	-78	—
Magnesium	MgO	solid	40.32	—143.840	3530	0.66	1.43	5050	(2250)	very high
Aluminum	Al_2O_3	solid	101.94	—396.500	3900	0.855	1.66	6460	2700	(1137)
Silicon	SiO_2	solid	60.06	—203.300	3350	1.14	1.50	5030	1900	(1310)

Table IV.1

Properties of the Principal Combustible and Oxidizer Elements and of their Combustion Products

Name of Elements	Symbol or Formula	Phase	Molecular Weight	Specific Gravity, γ, kg/ltr	Melting Point t_{melt}, °C	Boiling Point t_{boil}, °C
Hydrogen	H_2	liquid	2,016	0,07	—257,14	—252,79
Lithium	Li	solid	6,941	0,534	180	1400
Beryllium	Be	solid	9,01	1,85	1280	—
Boron	B	solid	10,82	1,73	2300	—
Carbon	C	solid	12,01	2,25	—	—
Magnesium	Mg	solid	24,32	1,74	650	1120
Aluminum	Al	solid	26,97	2,70	658	(2000)
Silicon	Si	solid	28,06	2,35	1414	(2400)
Oxygen	O_2	liquid	32,00	1,14	—223	—187
Fluorine	F_2	liquid	38,00	(1,14)	—218	—183

Fluorine Combustion Products

Name of Elements	Symbol or Formula	Phase	Molecular Weight	$\Delta H^0_{298.16}$ kcal/gm-mole	Kcal/kg	No kg/kg	γ kg/ltr	Kg kcal/ltr	t_{boil} °C	ΔH_{evap} kcal/kg
Hydrogen	HF	gas	20,008	—64,20	3210	9,46	0,46	1475	19	—
Lithium	LiF	solid	25,94	—146,3	5650	2,74	0,87	4930	1680	(1960)
Beryllium	BeF₂	solid	47,01	—227,0	4930	4,22	1,23	5950	(1300)	(850)
Boron	BF₃	gas	67,82	—265,4	3910	5,26	1,21	4750	—101	—
Carbon	CF₄	gas	88,01	—162,5	1850	6,32	1,22	2250	—128	—
Magnesium	MgF₂	solid	62,32	—263,5	4210	1,56	1,31	5550	(2230)	(1110)
Aluminum	AlF₃	solid	83,97	—311,0	3710	2,12	1,41	5220	(1260)	(1100)
Silicon	SiF₄	gas	104,06	—361,3	3470	2,79	1,33	4600	—95	—

15

hydrogen as a rocket fuel.

The boiling points of the oxides, except for water and carbon dioxide gas, are very high, and the heat of vaporization has an excessive value, sometimes even greater than the heat of formation of the solid product. The use of fuels based on metallic combustibles and oxygenic oxidizers may prove inadvisable, since the combustion process at a high temperature involves a low liberation of energy because of dissociation, while the combustion process at a low temperature demands the presence of a gas phase to absorb the heat of the solid particles. The high molecular weights of the combustion products predetermine the high temperatures in the combustion chamber during combustion of metals.

Among the fluorine compounds of the combustible elements, hydrogen fluoride HF and carbon tetrafluoride CF_4 have the lowest heats. For HF this is the same as for water; for CF_4, it is lower than that of carbon dioxide CO_2. In addition, the molecular weight of CF_4 is very high. For this reason, the use of fluorine as an oxidizer for hydrocarbon combustibles is inadvisable.

It must, however, be borne in mind that the diatomic molecule HF is considerably more stable against dissociation than the triatomic molecule H_2O. For this reason, for very hydrogen-rich combustibles, the use of fluorine oxidizers may prove expedient, owing to the reduction of the losses connected with dissociation (cf. later in text).

The fluorine compounds of the remaining elements have a high heat of formation, per unit weight as well as per unit volume. Among them, lithium fluoride with its maximum weight has a heat of formation of very special interest.

Attention is attracted to the fact that all fluorine compounds of metals have a considerably lower boiling point than the oxygen compounds and, no less important, a relatively low heat of vaporization. Due to this fact, the use of fluorine oxidizers for metallic combustibles may have considerable advantages over oxygen oxidizers. Among the fluorine compounds LiF and BeF_2 have satisfactory molecular weights.

2. Modern Fuels for Liquid-Fuel and Powder Propellant Rocket Engines

Requirements to be Met by Liquid Fuels

Besides the above-enumerated requirements for rocket fuels in general, the practical use of fuel in a liquid-fuel rocket engine results in many other requirements large in number and, unfortunately, difficult to satisfy. Let us consider the principal ones.

Most rocket fuel components are chemical compounds. Every chemical compound may be formed from its elements, with either absorption or liberation of heat.

Assume that a certain chemical compound, used as a fuel component, has a negative heat of formation, i.e., liberates heat on its formation. In order to liberate the combustible and oxidizer elements from this substance in the combustion chamber, it will obviously be necessary to consume, on account of the heat of combustion, an additional energy equal to the heat of formation of the components. If a compound used as a fuel component has a negative heat of formation, then the quantity of heat obtained in the combustion chamber is reduced accordingly. At a positive heat of formation of the fuel component, the heat value of the fuel is increased over the heat value of the elements taken in the standard state.

It follows from the above that the fuel components must have positive heats of formation. The proposals to utilize combustibles in the atomic state for liquid-fuel rocket engines are based precisely on this principle.

The requirements resulting from the conditions of the cooling of the engine are that the fuel components must be able to absorb the largest possible quantity of heat or, conventionally expressed, that they have the maximum heat absorptivity.

Numerically, the heat absorptivity of a component is

$$Q = c \, (T_{boil} - T_0) \text{ kcal/kg}$$

where c is the heat capacity of the component;

T_{boil} is the boiling point of the component under the pressure that exists in the cooling jacket (for a description of the cooling system, see below);

T_0 is the temperature of the component equal to the temperature of the ambient medium.

A component with a greater heat absorptivity and a higher boiling point will have a higher heat absorptivity.

The heat absorptivity of a component is most correctly related to 1 kg of fuel burned in the engine, since both the quantity of heat liberated in the engine and the quantity of substance used for cooling are proportional to the total consumption of fuel, and not to the consumption of the individual components.

The specific heat absorptivity of a combustible is

$$Q_c = C_c (T_{boil} - T_0) \frac{1}{1 + v} \text{ kcal/kg fuel;}$$

while the specific heat absorptivity of an oxidizer is

$$Q_c = c_o (T_{boil} - T_0) \frac{v}{1 + v} \text{ kcal/kg fuel}$$

With the same physical properties (heat capacity and boiling point) an oxidizer will have a higher specific heat absorptivity than the combustible, since $v > 1$. For this reason, if a high-boiling oxidizer is used in a liquid rocket engine, this oxidizer will, as a rule, be used as the liquid used for cooling.

The total heat absorptivity of the coolant component QG (where G is the weight consumption of fuel in unit time) must be greater than the total quantity of heat to be removed from the cooling surfaces of the engine per unit time. If this condition is not satisfied for any of the fuel components taken separately, then the engine must be cooled by both components at the same time.

The conditions of fuel feed result in the requirement that the viscosity of the components as well as temperature dependence of their viscosity be low. Otherwise, a variation in the temperature of the ambient medium may lead to a variation in the

ratio v of the components supplied to the chamber and to less favorable fuel utilization.

The conditions of ignition and combustion of the fuel in the engine chamber demand a low ignition point for fuels that are not of the igniting type, and the smallest possible period of ignition lag for self-igniting fuels. The latter requirement is of the greatest importance.

The self-ignition lag means the time elapsing from the moment of contact between the liquid components of a self-igniting fuel to its ignition. Sometimes this quantity is called the induction period. It is clear that, with chemical ignition, the quantity of fuel accumulated in the combustion chamber when the engine is started (other conditions being equal) will be greater, the longer the self-ignition lag. As noted above, the accumulation of the mixture in the chamber may lead to explosion of the engine. From the condition of safe starting, the self-ignition lag must not exceed 0.03 sec.

For reliable engine starting under various meteorological conditions and at various altitudes, the self-ignition lag must not increase excessively as the temperature of the fuel and the atmospheric pressure decrease.

The operating conditions of engine and rocket require the fuels to possess physical and chemical stability, which will permit storage of the components for prolonged periods without special precautions, will ensure safety from explosion and will ensure high boiling points and low freezing points. The fuel must not be toxic and must not attack the structural materials. The rocket fuel must also be cheap, it must be possible to produce it on a large scale, and raw materials must be available for its production.

It must be said that there are still no fuels that simultaneously satisfy all these requirements.

Today, in spite of the extensive investigations in the field of new substances, a rather limited number of chemical compounds are being used as fuels.

Classification of Rocket Fuels

Rocket fuels may be classified according to various criteria.

First of all we must distinguish the physical state of the fuel. According to this criterion, fuels are divided into liquid and solid (powder) fuels. Mixed fuels are an intermediate group, one component being a liquid, the other a solid. Numerous attempts to utilize such fuels in liquid-fuel rocket engines have been made. An example is the well-known use in rocket engines of jellied gasoline and charcoal rods placed directly in the combustion chamber, with the liquid oxidizer supplied from tanks.

Fuels may be classified according to the number of their components.

To simplify the feed system and the engine head design, the most expedient is the monopropellant (single-component fuel) containing both the combustible and oxidizer elements. Such fuels have actually been developed, but until now not a single monopropellant with a high heat value, that would be safe and reliable in operation, is known. All fuels used today are of the bipropellant or two-component type.

The third method of classification is their division, with which we are already familiar, into non-self-igniting and self-igniting.

Figure 4.2 gives a system of fuel classification.

The properties of a propellant are determined primarily by the properties of the oxidizer. Therefore propellants are also classified into groups according to the type of oxidizer used. For this reason, we will start the following description of fuels with a description of the properties of the oxidizers.

The properties of the oxidizers, combustibles, and of the propellants as a whole are given in Tables IV.2, IV.3, and IV.4. These Tables indicate the elementary composition, i.e., the content of elements: carbon C, hydrogen H, oxygen O, and nitrogen N in 1 kg of oxidizer or combustible, the heat of formation, the specific gravity, the melting point (or freezing point), and the boiling point. For fuels we show the heat values per unit volume and weight, the gas formation, the approximate
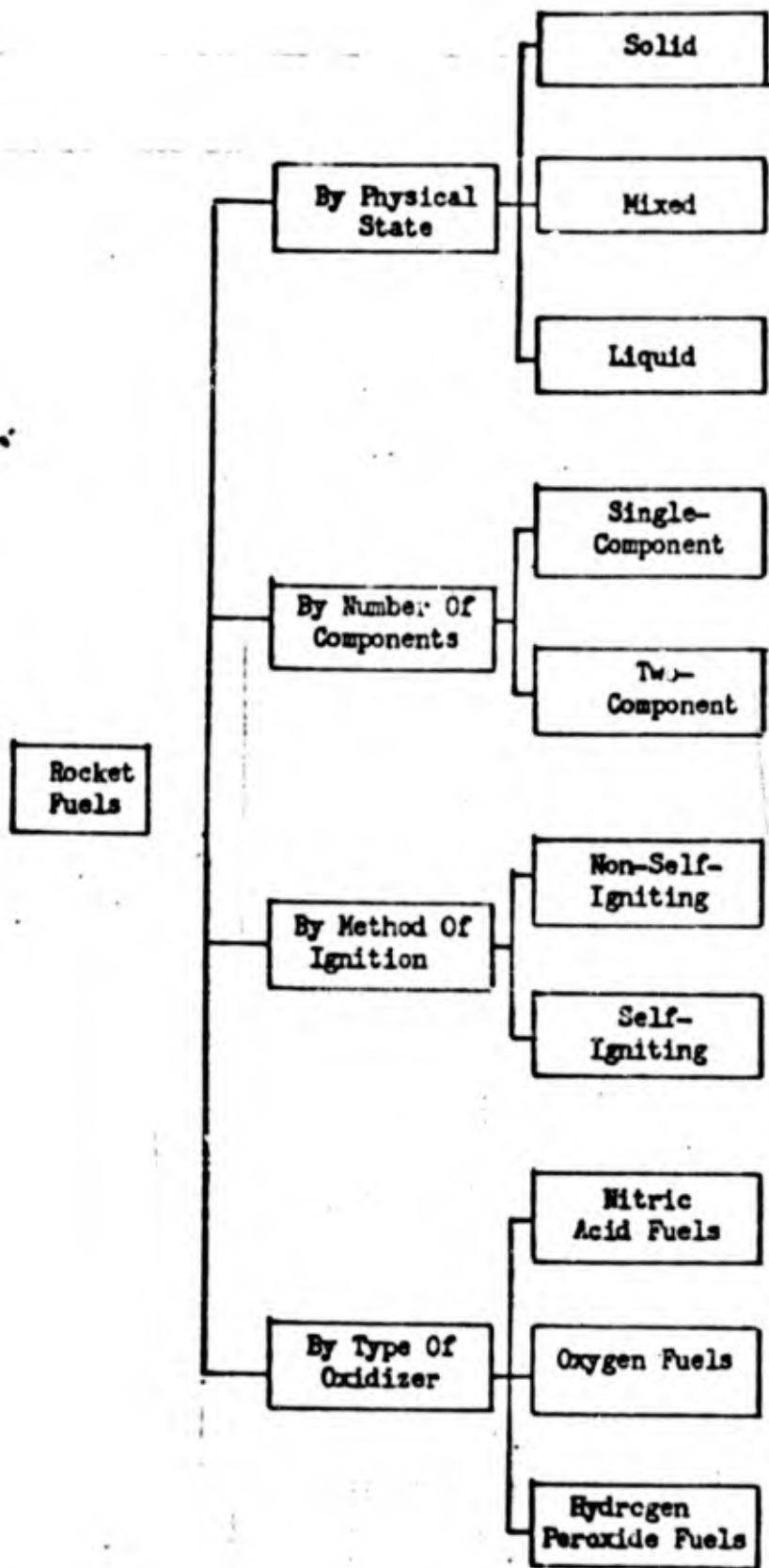
Fig.4.2 - Classification of Rocket Fuels

temperature in the combustion chamber, and the approximate thrust for a rocket engine with average parameters.

Nitric Acid and the Nitrogen Oxides. Tetranitromethane

Nitric acid HNO_3 is a product widely used in the national economy. Its large-scale production had been established before the appearance of liquid-fuel rocket engines. It is precisely for this reason that it was used as oxidizer in the first liquid-fuel rocket engines. Propellants based on nitric acid are widely used in rocket engineering today.

In the pure form, nitric acid is a colorless liquid. Technical nitric acid always contains a certain quantity of water and of nitrogen oxides, which give the technical acid a reddish-brown color.

The presence of water in nitric acid is undesirable, since it lowers the heat value of the fuel. Acid of 98 - 96%, i.e., with a water content not over 2 - 4%, is therefore used for rocket engines.

Pure nitric acid (cf. Table IV.2) contains 76% of oxygen and has a low negative heat of formation. This makes it a relatively powerful oxidizer. Of all the extensively used oxidizers, nitric acid has the highest specific gravity, which permits the preparation of a fuel with a high heat value per unit volume.

Nitric acid has a boiling point (+86°C) and a freezing point (-42°C) which are very favorable for its use in a liquid-fuel rocket engine. The addition of up to 10% of water to HNO_3 lowers the freezing point somewhat (to -68.5°C). On further dilution of nitric acid, the freezing point rises.

The boiling point of HNO_3 increases with the pressure, so that under the pressures that exist in the cooling jacket of liquid-fuel jet engines, the boiling point exceeds 200°C.

The heat capacity of HNO_3 is about 0.5 kcal/kg deg which, in conjunction with the high boiling point and the high content of nitric acid in the propellant

Table IV.3

Principal Data of Combustibles for Modern Liquid-Fuel Rocket Engines

Name	Chemical Formula	Molecular Weight	Elementary Composition				Heat of Formation, kcal/gm-mole	Specific Gravity, kg/ltr	Boiling Point* °C	Melting Point* °C
			C	H	O	N				
Tractor kerosene	—	100	0,858	0,135	0,007	—	—46,0	0,76÷0,84	170÷180	—50
Ethanol	C₂H₅OH	46,07	0,522	0,131	0,347	—	—69,90	0,798	78,5	—117,3
Methanol	CH₃OH	32,04	0,375	0,125	0,500	—	—60,24	0,791	64,6	—97,9
Aniline	C₆H₅NH₂	93,08	0,774	0,176	—	0,150	+7,98	1,022	184,4	—6,2
Triethylamine	(C₂H₅)₃N	101,07	0,712	0,149	—	0,139	—?,2	0,728	89,5	—114,8
Xylidene	(CH₃)₂C₆H₃NH₂	121,12	0,792	0,092	—	0,116	—46,2	—	—	—
Furfuryl alcohol	C₄H₃OCH₂OH	98,06	0,613	0,062	0,325	—	—63,1	1,13	171	—32
Hydrazine hydrate	N₂H₄·H₂O	50,06	—	0,122	0,318	0,560	—63,13	1,03	118,3	—40
Vinyl ethyl ether	C₂H₃OC₂H₅	72,07	0,667	0,111	0,222	—	—46,0	0,754	36	—50

* Under atmospheric pressure

Table IV.2

Principal Data of Pure Oxidisers for Modern Liquid-Fuel Rocket Engines

Name	Chemical Formula	Molecular Weight	Elementary Composition				Heat of Formation, kcal/gm-mole	Specific Gravity, kg/ltr	Melting Point*	Boiling Point***
			O	C	H	N				
Nitric acid	HNO₃	63,02	0,762	—	0,016	0,222	—11,66	1,51	—41,6	+86
Nitrogen tetroxide	N₂O₄	92,02	0,696	—	—	0,304	+8,0	1,47	—9,3	+22
Tetranitromethane	C(NO₂)₄	196,04	0,653	0,061	—	0,286	+5,2	1,65	+13,8	+126
Liquid oxygen	O₂	32,00	1,000	—	—	—	0	1,14*	—227	—183
Hydrogen peroxide	H₂O₂	34,02	0,940	—	0,060	—	—45,20	1,46	0	+152
Water (in the liquid state)**	H₂O	18,02	0,889	—	0,111	—	—68,35	1,00	0	+100

* At a temperature of 183°C.

** Water enters into the oxidiser as ballast.

*** Under atmospheric pressure.

Table IV.4

Principal Data of Propellants for Modern Liquid-Fuel Rocket Engines

Oxidiser	Combustible	KG, kcal/kg	Y kg/ltr	Kv kcal/ltr	V ltr/kg	T* °abs	P spec* kg-sec/kg
Nitric acid, 98%	Kerosene	1460	1,36	1980	800	3000	220
Nitric acid, 98%	Tonka 250	1500	1,32	1800	784	2980	225
Nitric acid, 98%	Aniline (80%) + furfuryl alcohol (20%)	1520	1,39	1900	756	3050	223
Nitrogen tetroxide	Kerosene	1560	1,38	2000	680	3250	234
Tetranitromethane	Kerosene	1620	1,47	2200	660	3300	238
Hydrogen peroxide, 80%	Hydrogen Peroxide, 80%	680	1,35	920	1083	550	90÷100
Hydrogen peroxide, 80%	Methanol (50%) + hydrazine hydrate (50%)	4020	1,30	1330	940	2600	190
Liquid oxygen	Kerosene	2200	1,00	2200	650	3550	260
Liquid oxygen	Ethanol, 93.5%	2020	0,998	2000	789	3250	240

* The values of the combustion temperature T and the specific thrust P_{spec} are approximate (for orientation purposes) for the mean data of Liquid-fuel rocket engines at a 30:1 ratio of the pressure in the chamber to the pressure at a cross section of the nozzle.

$(v_o = 5.47)$, makes nitric acid a high-grade coolant with a high heat absorptivity.

Nitric acid also has a number of disadvantages. Its vapor is toxic, and when it comes into contact with the skin nitric acid causes severe burns. Therefore, working with it requires safety measures.

Nitric acid is highly aggressive toward metals and other structural materials. Nitric acid diluted with water has a particularly powerful action on metals. Therefore, flushing of engines and of parts after contact with it must be very thorough. Stainless steel and some plastics withstand its action.

Nitric acid readily evaporates, which leads to certain inconveniences in its storage.

To improve the properties of nitric acid as an oxidizer, various additives are added. These may be added to increase the calorific value of the propellant, to raise the specific gravity of the oxidizer, to decrease its aggressiveness against structural materials, to increase the activity of the oxidizer with respect to the combustible (especially with respect to combustibles that spontaneously ignite with nitric acid), and, finally, to decrease the freezing point of the propellant components. Many additives change not only one property of nitric acid, but several, i.e., exert a combined action.

Nitrogen tetroxide, sulfuric acid, and other substances are used as additives to nitric acid.

Nitrogen tetroxide N_2O_4 is an oxygen-rich nitrogen oxide with a positive heat of of formation. Liquid nitrogen tetroxide is yellow and evaporates easily. Its vapor decomposes in the air, and has a pronounced yellow color. The use of pure N_2O_4 as an oxidizer is impossible, owing to its high freezing point (-9.9°C) and its low boiling point (+22°C). It is therefore used only as an additive to nitric acid, to increase the calorific value of the propellant. The addition of N_2O_4 to HNO_3 also yields a solution with a higher specific gravity than those of pure nitrogen tetroxide or nitric acid, taken separately. The maximum specific gravity of such a solu-

30

tion, containing 40% of N_2O_4, is 1.63 kg/ltr. The addition of N_2O_4 likewise increases the activity of the oxidizer and, consequently, facilitates the starting of the liquid-fuel rocket engine.

The addition of nitrogen tetroxide to nitric acid, just like the addition of water, changes the freezing point of the mixture. The lowest freezing point (-73°C) is obtained on addition of 18% of N_2O_4. A further increase in the addition of N_2O_4 leads to a rise in the freezing point.

Concentrated sulfuric acid H_2SO_4 is used as an additive to decrease the aggressive properties and to improve the starting conditions of the engine, especially with self-igniting propellants. Mixtures of nitric and sulfuric acids are called melanges. A disadvantage of adding sulfuric acid to nitric acid is the lowering of the heat value of the propellant.

Ferric chloride is added to nitric acid with the object of lowering the freezing point and increasing the activity of the acid.

Besides HNO_3 and N_2O_4, among the nitrogen compounds of oxygen, tetranitromethane $C(NO_2)_4$ may also be used as an oxidizer. Tetranitromethane has a positive heat of formation. A great advantage of tetranitromethane as an oxidizer is its high specific weight (1.65 kg/ltr), which is greater than that of nitric acid. Tetranitromethane displays no aggressive action against structural materials. The use of tetranitromethane is limited by its tendency to explode. In addition, it is also strongly toxic, acting on the human mucous membranes.

The freezing point of tetranitromethane is rather high: $+13.8^\circ$C, but when mixed with N_2O_4, its freezing point is lowered to -26°C, which permits the use of this mixture as an oxidizer for liquid-fuel rocket engines.

Fuels Used in Propellants Based on Nitric Acid or Nitrogen Oxides

Kerosene is the fuel component most widely used for propellants based on nitric acid or nitrogen oxides. Table IV.3 gives the principal physicochemical properties

of kerosene, and Table IV.4, the properties of the propellant nitric acid + kerosene.

The successful use of kerosene in liquid-fuel rocket engines is promoted by a considerable number of favorable qualities of this fuel component. Propellants containing kerosene have a high calorific value. Kerosene remains liquid over a wide range of temperatures. It may be utilized for cooling the engine: its heat content is 0.45 kcal/kg deg, and its boiling point at elevated pressures reaches 250°C. The transportation and storage of kerosene causes no difficulties, and its production is ensured by the broad development of the petroleum refining industry.

Kerosene may be used as a propellant component, with all oxidizers based on nitrogen oxides. The calorific value of a propellant of nitric acid plus kerosene is 1460 kcal/kg. For nitrogen oxides it is somewhat higher (1500 kcal/kg), because of the better qualities of the oxidizer. A shortcoming of kerosene is its relatively low specific weight (0.80 - 0.85 kg/ltr). A mixture of kerosene and nitric acid, as well as other propellants based on kerosene and nitrogen oxides, are not self-igniting and require forced ignition.

Other hydrocarbons which, in the vapor form, yield non-self-igniting propellants with nitric acid, for instance alcohols, have not found application in liquid-fuel rocket engines.

Self-igniting fuels have also been created on the base of nitric acid and nitrogen oxides. The combustibles in such propellants are usually complex hydrocarbons: aniline $C_6H_5NH_2$, furfuryl alcohol $C_4H_3OCH_2OH$, xylidene $(CH_3)_2C_6H_3NH_2$, triethylamine $(C_2H_5)_3N$. Their composition and principal physicochemical properties are given in Table IV.3. Of the peculiar properties of these hydrocarbons, only the somewhat higher specific gravity of aniline (1.03 kg/ltr) needs to be pointed out.

To obtain the shortest possible self-ignition lag, at otherwise satisfactory properties, optimum mixtures of propellants consisting of various substances are selected. This encompasses a large number of self-igniting propellants of various compositions. Their common shortcoming is the high cost and short supply of their

components. Such self-igniting mixtures are used in practice not only as the principal propellant of the engine, but also as igniters in chemical ignition systems.

The most widely used self-igniting propellants are the following mixtures:

1. Nitric acid + a combustible consisting of 50% xylidene and 50% triethylamine*.

2. Nitric acid + a combustible consisting of 80% aniline and 20% furfuryl alcohol.

Liquid Oxygen

Liquid oxygen is an even more powerful oxidizer than nitric acid, since it contains 100% oxidizing element. Liquid oxygen is a bluish transparent liquid, boiling at -183°C. Its specific gravity is considerably lower than that of nitric acid, being 1.14 kg/ltr at its boiling point. The low boiling point of liquid oxygen prevents its use as a coolant. For this same reason, oxygen is unsuitable for use in rockets that must be kept in the ready filled state. The tanks of the rocket are filled with liquid oxygen immediately before launching. Even under this condition there are considerable losses of oxygen by evaporation.

Liquid oxygen is relatively harmless to human beings. If spilled on the skin in small quantities, liquid oxygen boils, and the layer of gaseous oxygen thus formed protects the skin from freezing.

In recent years liquid oxygen has come into intensive use in many fields of technology, so that its large-scale production has been started. The problems of storing and shipping liquid oxygen have also been satisfactorily solved. For this reason, despite the unavoidable losses due to evaporation (when used in liquid-fuel rocket engines, about 50% of the initial quantity of oxygen is lost), the cost of the liquid oxygen used in rockets is low.

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* A mixture of xylidene and triethylamine is called "Tonka 250".

Combustibles for Propellants Based on Liquid Oxygen

Any hydrocarbon may be used as combustible for liquid oxygen. All yield non-self-igniting propellants with liquid oxygen. A mixture of liquid oxygen and kerosene has a high heat value, equal to 2200 kcal/kg. This is the most powerful of all modern liquid fuels. Attempts to use a mixture of oxygen and kerosene were made at the very dawn of the development of rocket engineering. The difficulties of using this mixture in a liquid-fuel rocket engine are due to the high temperature of combustion as well as to the very small amount of kerosene in the fuel (about 20%) which complicates cooling of the engine. Up to now, this has limited the use of oxygen in the vapor phase with kerosene.

Propellants with liquid oxygen as oxidizer and with ethyl or methyl alcohol as combustible are widely used at the present time.

Table IV.3 gives the principal indices of ethanol and methanol. In technology, ethyl alcohol of 93.5% concentration is used. To prepare an alcohol of higher concentration involves too complex a procedure. The heat value of alcohols is lower than that of kerosene, since they have a high negative heat of formation, but, on the other hand, the temperature of combustion of the alcohol in oxygen is lower. This facilitates the creation of a reliably operating engine. The specific gravity of these alcohols is low (0.8 kg/ltr). The boiling point is rather high (taking account of the pressure in the cooling jacket of a liquid-fuel rocket engine), which permits the use of the alcohol as a coolant. The heat capacity of alcohol is somewhat higher than that of kerosene, and is about 0.6 kcal/kg deg. Owing to the fact that the alcohol itself contains a considerable amount of oxygen, the relative proportion of the alcohol in the fuel is increased to 40 - 45%. This likewise favors successful cooling of the engine by the alcohol.

Ethyl and methyl alcohols are miscible in all proportions with water. This permits ready preparation of fuels of various heat values, thus reducing the temperature in the combustion chamber and increasing the total heat absorptivity of the

combustibles to any desired degree. This was exactly the trend followed by designers of the first ballistic rockets, using a 75% aqueous solution of alcohol as the combustible, although the specific thrust of the engine was considerably reduced in this case (to 204 kg sec/kg).

The low freezing point of the alcohol permits its use over a wide ambient temperature range.

Alcohol is produced in very large quantities and is not a combustible in short supply. It has no aggressive action on the structural materials. This makes it possible to use tanks and pipelines of relatively inexpensive materials for alcohol.

Methyl alcohol can be used as a substitute for ethyl alcohol. Together oxygen, it gives a fuel somewhat poorer in quality. Methyl alcohol is miscible with ethyl alcohol in any proportions, which allows it to be used in the absence of adequate ethyl alcohol, and permits its addition in certain proportions to the combustible. Propellants on the basis of liquid oxygen are used almost exclusively in long-range rockets; this allows and, because of their high weight, actually demands filling of the rocket with the components at the launching pad.

Hydrogen Peroxide

Hydrogen peroxide H_2O_2 in the pure state (i.e., 100% conc) is not used in technology, since it is a highly unstable product, tending toward spontaneous decomposition, which easily results in an explosion under the influence of any, apparently insignificant, external influence: percussion, illumination, slightest contamination by organic substances, and impurities of certain metals.

In rocket engineering, more stable high-concentration solutions of hydrogen peroxide and water (most often 80% conc) are used. To increase the stability, small quantities of substances preventing the spontaneous decomposition of hydrogen peroxide are added (for example, phosphoric acid). At present, the use of 80% hydrogen peroxide requires only the usual safety measures as necessary in handling strong

oxidizers. Hydrogen peroxide of such concentration is a transparent slightly bluish liquid with a freezing point of $-25^{\circ}C$.

Hydrogen peroxide liberates heat on its decomposition into oxygen and water vapor. This liberation of heat is explained by the fact that the heat of formation of the peroxide is 45.20 kcal/gm-mole, while the heat of formation of water is 68.35 kcal/gm-mole. Thus, on decomposition of hydrogen peroxide according to the formula $H_2O_2 = H_2O + 1/2\ O_2$, the chemical energy liberated is equal to the difference $68.35 - 45.20 = 23.15$ kcal/gm-mole, or 680 kcal/kg.

Hydrogen peroxide of 80% conc is able to decompose in the presence of catalysts, liberating 540 kcal/kg of heat and evolving free oxygen, which may be utilized for the oxidation of a combustible. Hydrogen peroxide has a relatively high specific gravity (1.36 kg/ltr for 80% conc). Hydrogen peroxide cannot be used as a coolant, since it does not boil on heating but decomposes immediately.

Stainless steel and very pure aluminum (impurities not over 0.5%) can be used as materials for the tanks and pipelines of engines operating on peroxide. The use of copper and other heavy metals is entirely impermissible. Copper is a powerful catalyst encouraging the decomposition of hydrogen peroxide. Certain forms of plastics may be used for gaskets and seals. Concentrated hydrogen peroxide causes severe burns when it comes in contact with the skin. Organic substances inflame on contact with hydrogen peroxide.

Propellants Based on Hydrogen Peroxide

Two types of propellants have been developed on a hydrogen peroxide base.

Propellants of the first type are propellants whose components are fed separately in which the oxygen liberated on decomposition of the hydrogen peroxide is used for igniting the combustible. The propellant used in the engine of the interceptor aircraft described above (see Chapter III), can serve as an example. This propellant consisted of 80% hydrogen peroxide and a mixture of hydrazine hydrate

($N_2H_4 \cdot H_2O$) with methyl alcohol. On adding a special catalyst to the combustible, this fluid becomes self-igniting. The relatively low calorific value (1020 kcal/kg), as well as the low molecular weight of the combustion products, results in a low combustion temperature which facilitates engine operation. Because of the low calorific value, however, the engine has a low specific thrust (190 kg sec/kg).

With water and alcohol, hydrogen peroxide can form relatively explosion-safe ternary mixtures, which are typical examples of a monopropellant. The heat value of such explosion-safe mixtures is relatively low: 800 - 900 kcal/kg. For this reason, it is not very suitable as the principal fuel for a liquid-fuel rocket engine. However, such mixtures may be used in steam-gas producers.

The reaction of decomposition of concentrated peroxide, as already stated, is widely used in rocket engineering to prepare steam-gas, which is the working medium of the turbine in pump delivery.

Engines are also known in which the heat of decomposition of the peroxide is used for producing thrust. The specific thrust of such engines is low (90 - 100 kg sec/kg).

Two types of catalysts are used for decomposing peroxide, liquid (a solution of potassium permanganate $KMnO_4$) or solid. The use of a solid catalyst is preferable, since the system for feeding the liquid catalyst to the reactor can be eliminated in this case.

Rocket Powders

Rocket powders are the solid fuel used in powder rocket engines. In addition to the principal requirements that all rocket fuels must meet, powder must also meet the following demands:

1. The powder must burn stably at low pressures in the chamber. This requirement is of considerable importance in connection with the fact that the combustion chamber of a powder engine represents at the same time the reservoir containing all

the fuel. At high pressure, the required great thickness of the walls results in a high weight for the chamber and a high value of the p_K of the rocket.

2. The powder must have high chemical stability. This is required because of the fact that the powder is subjected to the action of pressure in the combustion chamber and to considerable inertia loads. The rupture of the powder grains during combustion leads to an increase in the combustion surface, an increase in pressure in the chamber, and to explosion of the engine.

Some other requirements that powders must meet will be indicated below, in the chapter devoted to the combustion of fuels.

A modern rocket powder consists of a solution of two or several organic nitro compounds.

The principal substance entering into the composition of a powder and ensuring the necessary physical properties of a powder is nitrocellulose.

Nitrocellulose (cellulose nitrate) is prepared by treating cellulose, i.e., organic fibrous substances (wood cellulose or cellulose prepared from cotton), with concentrated nitric acid. For this purpose, stacks of cellulose are dipped in a vat of nitric acid. By such treatment, the cellulose is converted into complex organic esters containing nitrogen and oxygen.

The liquid substance dissolving nitrocellulose and ensuring its gelling (i.e., the preparation of a solid solution of uniform composition and uniform physicochemical properties) is nitroglycerin. It is the second principal substance entering into the composition of powder. Nitroglycerin is prepared by treating glycerol with a mixture of concentrated nitric and sulfuric acids. A molecule of nitroglycerin [chemical formula $C_3H_5(ONO_2)_3$] contain a considerable quantity of the oxygen necessary for combustion of the combustible elements carbon and hydrogen. The heat value of nitroglycerin is 1485 kcal/kg. Nitroglycerin is the principal substance of powder, having a reserve of chemical energy. Its percentage determines the heat value of the powder.

At normal temperatures, nitroglycerin is a heavy oily liquid (specific gravity 1.6 kg/ltr). Pure nitroglycerin is colorless, while the technical product has a slightly yellow tinge. With rising temperature, nitroglycerin gives off a faint sweetish odor. Its vapor is toxic and causes headache, while large doses entering the human organism may cause poisoning.

Glycerol, which is the starting material for the preparation of nitroglycerin, demands the consumption of fats for its production. For this reason, the attempt is made in the production of rocket powders to replace nitroglycerin, though only in part, by other gelling substances. Diethyl phthalate, dinitrotoluene, diethylglycol dinitrate, and certain other compounds are used as such substances.

Besides these principal substances, small amounts of various additives are also introduced into rocket powders.

To give the powder chemical stability, substances like diphenylamine and centralite are added to it. These substances, which prevent the decomposition of the powder, also prevent changes in the physical properties and structure of the powder. Changes in the structure of the powder during storage are extremely undesirable, since they may lead to a disturbance of normal combustion and to explosion of the engine. Certain additions (vaseline or wax) serve to give the powder mass the plasticity required in the technology of manufacturing the powder grains.

Since a rocket powder is a mixture of various substances, the heat value of such a powder is determined by the composition and heat of formation of its components.

Nitrogen, which plays the role of a binder, uniting into a single molecule the combustible and oxidizer elements, acts as ballast in powders as it does in liquid fuels. For this reason a high content of nitrogen leads to a reduction in the heat value of the powder. The nitrocellulose used for powders ordinarily contains 12 - 14% of nitrogen.

The heat value of a powder is likewise determined by the value of the so-called oxygen balance, i.e., by the value of v for the powder or its components. For most

Table IV.5

Composition and Properties of Various Rocket Powders

Powder	Composition		Heat Value K_G, kcal/kg	Combustion Temperature at Constant Pressure, T^0 abs	Reduced Force of Powder f_0, kg-m/kg
	Type of Substance	Content, in wt.%			
I.P.	Nitrocellulose (13.25% N_2)	52.2	1230	3170	100,000
	Nitroglycerin	43.0			
	Diethyl phthalate	3.0			
	Diphenylamine	0.6			
	Potassium nitrate	1.1			
	Nigrosine	0.1			
I.P.N	Nitrocellulose (13.25% N_2)	51.50	1230	3170	100,000
	Nitroglycerin	43.00			
	Diethyl phthalate	3.00			
	Centralite	1.00			
	Potassium sulfate	1.25			
	Gas carbon black	0.20			
	Candellia wax	0.05			
Slow-burning powder	Nitrocellulose (12.2% N_2)	56.5	880	2330	76,000
	Nitroglycerin	28.0			
	Dinitrotoluene	11.0			
	Centralite	4.4			
	Candellia wax	0.1			

powders, $v < v_0$ or, expressed differently, the powder has a negative oxygen balance, leading to a deficiency of oxygen ($\alpha < 1$) and incomplete combustion of the combustible elements.

Most of the components of rocket powders, except for diphenylamine, have a negative heat of formation.

Due to all these reasons (high nitrogen content, negative oxygen balance, and negative heat of formation of the components) a powder has a relatively low calorific value, ranging from 820 to 1250 kcal/kg, depending on the nitroglycerin content (or the content of other solvents).

As an energetic characteristic for a powder, the so-called reduced force of the powder f_0, kg-m/kg, is often used in addition to the calorific value.

The product of a gas constant R by the temperature of the combustion products T is called the force of a powder. Here the combustion temperature, in accordance with the conditions of combustion of the powder in the rocket engines, is taken at constant pressure.

The reduced force of a powder enters directly into the expression determining the exhaust velocity; therefore, in some cases it is more convenient for calculation than the calorific value.

Table IV.5 gives the composition and properties of several rocket powders.

Methods of Increasing the Chemical Energy Reserve in Fuels

The desire to increase the specific thrust of a liquid-fuel rocket engine leads to attempts to find new and more productive fuels. Many references are found in the literature on attempts to use ozone, fluorine and its compounds as new oxidizers and suspensions of metals in kerosene, compounds of boron with hydrogen, as well as a number of organometallic compounds as combustibles. However, no data on engines operating on such fuels are available.

As will be seen from the data in Table IV.1, even today there are a number of

possibilities of increasing the calorific value of rocket fuels. At the same time, these possibilities are limited by the considerable heat loss due to the dissociation of the combustion products at the high temperatures prevailing in the chamber (cf. infra, Chapter V), as well as by the difficulty of feeding solid substances into the engine. Great difficulties must be expected in any attempt to ignite solid substances, and also in the introduction of the highly toxic and aggressive fluorine oxidizers into rocket engineering.

The use of solid (metallic) combustibles can be imagined in the form of suspensions of finely divided metal in an ordinary combustible or in the form of organometallic and metal-hydrogen compounds which, under normal conditions, are liquids. Table IV.6 gives the physical properties of several organometallic and metal-hydrogen compounds (inadequately verified values of physicochemical constants are shown in parentheses).

In the literature on questions of rocket engineering, other methods of increasing the weight and volume calorific value of fuels are also considered.

Table IV.6

Properties of Certain Organometallic and Metal-Hydrogen Compounds

Type of Substance	Chemical Formula	Melting Point, ^{o}C	Boiling Point, ^{o}C	Heat of Formation, kcal/gm-mole	Specific Gravity, kg/ltr
Pentaborane	B_5H_9	(50)	(60)	(0)	(0,64)
Diboraneimine	B_2H_7N	—66	76	(—10)	(0,70)
Diethylberyllium	$Be(C_2H_5)_2$	12	(200)	(—35)	(0,60)
Trisilane	Si_3H_8	—117	53	(—20)	(0,88)
Trisilylamine	$(SiH_3)_3N$	—106	52	(+10)	0,895

The calorific value of fuels using chemical energy may be increased by using not the pure elements in their standard form as components but by using elements in the form of compounds which in themselves, in addition to the chemical energy of the

elements liberated on combustion, possess the positive heat of formation consumed during their preparation.

This heat is liberated at the time of the combustion reaction and is added to the chemical energy of the combustion products.

Typical examples of substances with a positive heat of formation are the combustible or oxidizer elements which are not in the standard molecular state but in the atomic state. In this case, an excessive quantity of energy is consumed on the formation of the atomic elements (see Table IV.7). Thus, 1 kg of atomic hydrogen

Table IV.7

Table of Substances with a Positive Heat of Formation

Type of Substance	Chemical Formula	Heat of Formation		Specific Gravity, kg/ltr
		kcal/gm-mole	kcal/kg	
Atomic hydrogen	H	51.6	51500	
Atomic oxygen	O	58.6	3640	
Ozone	O_3	35.0	730	1.71 at − 183°C
Acetylene	C_2H_2	54.85	2120	0.618 at -81.5°C
Tetranitromethane	$C(NO_2)_4$	16.0	81.5	1.65 at 20°C
Nitrogen tetroxide	N_2O_4	6.0	87.0	1.49 at 0°C

stores 51,500 kcal of heat. Up to now, however, no cases of the preparation of atomic hydrogen or atomic oxygen in pure form, nor of any prolonged storage of these substances, are known.

Another example is provided by substances as, for example, ozone O_3 which requires 730 kcal/kg for its formation from molecular oxygen, and acetylene C_2H_2 which is formed from carbon and hydrogen with a consumption of 2120 kcal/kg of heat.

A drawback of these substances is their low stability and their tendency to explode on storage and combustion, which makes it difficult to use them in engines. Only substances with a very low positive heat of formation, nitrogen tetroxide

N_2O_4 and tetranitromethane $C(NO_2)_4$ have found, or are finding, application in rocket engineering.

Attention is also called to the fact that many complex fuels and oxidizers have a specific gravity higher than those of the elements of which they consist. This is a favorable property, leading to an increase in the volume calorific value of the propellant.

3. The Energy of Nuclear Reactions and Its Utilization in Rocket Engines

a. The Atomic Nucleus and the Mass Defect

A further and quite considerable increase in the specific thrust of a rocket engine may be attained by using the energy of nuclear reactions, or so-called atomic energy.

Nuclear reactions, in contrast to chemical reactions, proceed in such a way as to modify the structure of the atoms.

According to modern views, the nucleus of the atom consists of heavy particles with a relatively great mass, of two forms: protons and neutrons. The proton is a positively charged particle having a mass almost equal to the mass of a hydrogen atom. The neutron, as indicated by its name, has no charge at all and its mass is likewise close to the mass of a hydrogen atom. The total number of protons and neutrons contained in the nucleus is called the mass number of the nucleus.

On formation of an atomic nucleus from free protons and neutrons, as in the formation of molecules from atoms, energy is liberated. The liberation of energy is due to the fact that the nuclei of elements represent a stable system bound by intranuclear forces, whose generation during the formation of the nucleus must be accompanied by a decrease in the potential energy of the system.

The energy of formation of a nucleus is most conveniently calculated by using the principle of the equivalence of mass and energy, according to which these quantities are connected by the relation

$$E = mc^2 \qquad (4.7)$$

where E is the energy;

m is the mass;

c is the velocity of light, which is 3×10^8 m/sec.

The energy equivalent to a mass of 1 kg-sec^2/m is 9×10^{16} kg-m. Converted into heat units, for 1 kg of weight, this gives

$$\frac{9 \times 10^{16}}{9.81 \times 427} = 2.15 \times 10^{13} \text{ kcal/kg}$$

It follows from the principle of equivalence of mass and energy that the interaction of the elementary particles of a nucleus forming a stable atom (with a negative potential energy) is accompanied by a decrease in their mass by comparison with the mass of the same particles separated by a distance excluding their interaction. This mass decrement Δm in nuclear reactions is known as the mass defect and may be determined experimentally. Based on the relation (4.7), the loss of energy of the system, which means the value of the energy liberated in this case is

$$E = \Delta mc^2$$

b. Nuclear Reactions

The energies of formation and, consequently, also the mass defects of different nuclei differ. For this reason, nuclear reactions leading to the formation of nuclei with a greater mass defect than the original nuclei are in principle possible. In this case, the newly formed nuclei will be more stable. The energy liberated on formation of a new nucleus is equivalent to the difference in mass defect between the newly formed and original nucleus.

Nuclear reactions proceed differently under the participation of different elements. Nuclear reactions with the participation of heavy elements having large mass numbers, take place most readily. It has been found that the higher the mass

number of a nucleus, the less stable will the nucleus be and the greater will be its tendency to disintegration. It is precisely the heavy nuclei of elements that possess the property of radioactivity, which is characterized by powerful radiation produced on fission of the nucleus.

Artificial nuclear reactions connected with the transmutation of light elements have likewise been known for long.

However, to obtain a high and constant energy yield in nuclear reactions, the nuclei must be artificially excited. The value of the energy of excitation in itself must be relatively high and, in addition, the exciting particle, carrying the necessary energy, must penetrate into the nucleus. Charged particles are unsuitable for intense excitation of nuclei, since the greater part of their energy is lost in overcoming the forces of the electric field surrounding the nucleus. The most suitable particles for the excitation of a nucleus are uncharged neutrons.

To sustain an uninterrupted nuclear reaction, it is necessary either to have an outside source of neutron radiation possessing the necessary energy reserve, or the nuclear reaction itself must be a source of neutrons for the excitation of an increasing number of nuclei. After the creation of such conditions, the practical utilization of the energy of the heavy nuclei first became possible.

c. The Problem of Utilizing the Energy of Nuclear Reactions in Rocket Engines

In considering the question of the possibility of utilizing the energy of nuclear reactions in rocket engines, two basic peculiarities of nuclear energy are encountered: its exceedingly high concentration and the necessity of having a so-called critical mass of active substance to accomplish certain nuclear reactions.

Let us first discuss the question of the concentration of atomic energy.

Each nuclear reaction is characterized by its energetic effect. The mass defect is taken as its measure and is expressed in fractions δ of the original mass of active substance. The value of δ is very small and is, of course, smaller than the

relative defects in the formation of the nuclei of the elements, since it is defined by the difference for two nuclei. Thus, for the reaction of fission of the nuclei of uranium* $_{92}U^{235}$, the value is $\delta = 0.000731$; in reactions with light atoms, the value of δ is considerably higher. For the formation of helium from lithium and hydrogen $_3Li^7 + _1H^1 \rightarrow 2_2He^4$, the value is $\delta = 0.00232$, and for the reaction of transformation of hydrogen into helium $4_1H^1 \rightarrow _2He^4$ it is $\delta = 0.00715$.

Even for such small mass defects, in view of the immense quantity of energy corresponding to unit mass, the energy yield K_G will be very great. On the basis of eq.(4.7), we have a value of $K_G = 2.15 \times 10^{13}\delta$ kcal/kg. For these reactions we will have:

Reaction	K_G, kcal/kg
Fission of uranium	1.57×10^{10}
$_3Li^7 + _1H^1 \rightarrow 2_2He^4$	2.67×10^{10}
$4_1H^1 \rightarrow _2He^4$	1.54×10^{11}

In the utilization of nuclear reactions in rocket engines, the energy liberated must be absorbed in the form of thermal energy by some working medium. Then, as in conventional engines, this energy must be transformed into kinetic energy. The working-medium selected must be a substance with a sufficiently high heat capacity per unit weight, i.e., as shown above, a substance with a small number of atoms in the molecule and the lowest possible molecular weight. Such substances (from among those that can possibly be used include primarily hydrogen H_2, then ammonia NH_3, and water H_2O, whose weight heat capacities are likewise relatively high.

It should be noted that the phenomenon of dissociation, which is harmful in the

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* In writing nuclear reactions, notations indicating the nuclear structure are used. The superscript of the symbol of the element denotes the mass number, while the subscript indicates the number of protons in the nucleus (atomic number).

Table IV.8

Quantity of Energy K_G Stored in 1 kg of Working Medium, and the

Corresponding Consumption of Active Mass G_a

Type of Working Medium	T = 4000° abs				T = 6000° abs			
	K_G, koal/kg	$G_a \times 10^{10}$, kg-sec/kg	P spec, kg-sec/kg	P' spec, kg-sec/ltr	K_G, kgal/kg	$G_a \times 10^{10}$, kg-sec/kg	P spec, kg-sec/kg	P' spec, kg-sec/ltr
Hydrogen H_2, undissociated	15500	7.20	822	57.6	25000	12.0	1045	78.2
Water H_2O, undissociated	2450	1.14	320	320	4700	2.18	453	453
Ammonia, on dissociation into H_2 and N_2	1940	0.90	293	200	3000	1.39	366	250
Atomic hydrogen H	71500	33.4	1105	—	81400	37.8	1320	—
Atomic oxygen O	4900	2.28	275	—	5500	2.56	357	—
Atomic nitrogen N	9500	4.42	298	—	10200	4.75	360	—

Note. The specific thrust is calculated for a ratio of 100 : 1
between the pressure in the chamber and the pressure at the discharge
from the nozzle. In calculating the specific thrust developed by
atomic substances, the recombination of atoms into molecules was not
taken into account.

utilization of chemical energy, may prove useful when nuclear energy is being
utilized since, on dissociation of the working medium, the nuclear energy may be
stored in the form of chemical energy of the dissociated gas.

The quantity of heat K_G stored in 1 kg of working medium at temperatures of
T = 4000 and 6000° abs (without taking dissociation into account) are given in
Table IV.8, which also shows the quantities of active substance (uranium $92U^{235}$ or
plutonium $94^{PU^{230}}$) necessary to heat 1 kg of working medium to the respective
temperatures.

It follows from the data of this Table that the quantity of active mass is very

small in comparison with the working medium. This, however, may involve substantial difficulties in designing heat exchangers for transfer of the energy to the working medium.

The thrust characteristics given in Table IV.8 indicate that a specific thrust considerably greater than in ordinary engines may be attained either by using hydrogen as the working medium or by considerably increasing the temperature of the working medium in the chamber.

The use of hydrogen is made difficult by its low specific gravity in the liquid state, and the necessity for increasing the temperature in the chamber poses a considerable number of problems connected with the difficulty of cooling.

The organization of the heat exchange, during which the energy will be transferred from the active mass to the working medium, is also an important problem.

The second problem relating to the utilization of atomic energy is that the presence of a certain minimum (or critical) mass is necessary in order for nuclear reactions to proceed. This requirement is explained by the fact that the size of the atomic nucleus is very small (the cross section of a nucleus is about 10^{-24} cm^2) and that, to ensure a sufficiently high probability of collision between the neutron and a nucleus, the mean free path of the neutron in the active substance must have a considerable length.

The value of the critical mass and the corresponding critical volume depend on the form of the active substance and the conditions under which the nuclear reactions take place. For the pure substances U^{238}, U^{235}, and Pu^{239}, the critical volume is equal to that of a sphere with a radius of several centimeters. The weight of such a sphere is 20 - 30 kg. In a rocket engine, however, it is difficult to expect the utilization of active substances in such small quantities, since under these conditions the heat-transfer surface would be very small.

To increase the heat-transfer surface, to slow down the velocity of a nuclear reaction, and to permit its control, a so-called moderator is added to the fis-

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sionable substance. A moderator must possess a low neutron-absorbing power, but must strongly decelerate the neutron. Graphite or heavy water is used as a moderator.

Such a system of utilizing the active substance is the foundation of all existing plans for utilizing atomic energy for industrial purposes. The value of the critical mass, when using a moderator, increases sharply and reaches a level of hundreds of kilograms.

Figure 4.3 shows the first of the possible systems for the layout of an engine working on atomic energy.

The liquid working medium (passive mass) is placed in the tank (1). The pump (2) supplies this fluid through the cooling jacket to the engine chamber. The con-
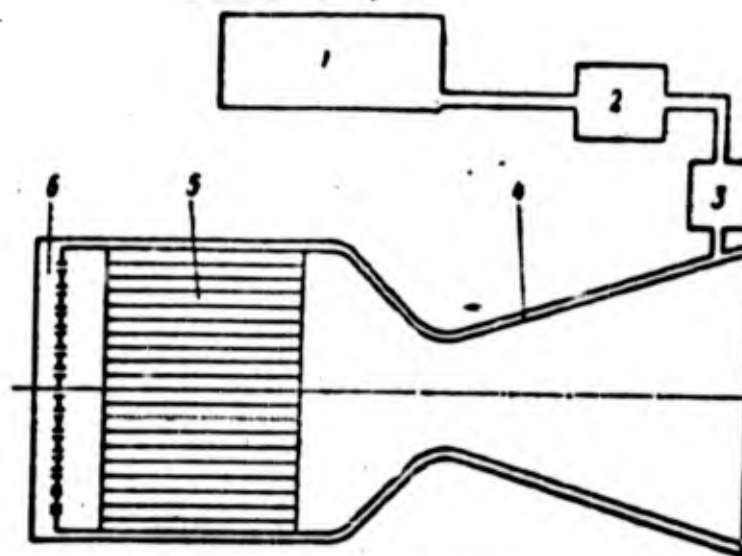
Fig.4.3 - Diagram of Atomic Rocket Engine with Packet of Solid

Active Substances

1 - Tank with liquid working medium; 2 - Pump; 3 - Instrument controlling supply of working medium; 4 - Cooling jacket; 5 - Packet of active substance (atomic fuel); 6 - Head with nozzles

trol instrument (3) is used for metering the discharge. On passing through the chamber head (6), the working medium comes into contact with the packet of reacting active substance, is heated to a high temperature, and then expands in the nozzle.

The principal difficulty in this system lies in the fact that the temperature

of the active substance, to ensure heat transfer to the working medium, must be very high, higher than the temperature of the working medium itself. The solution of this problem involves great difficulties, since we know of no material that remains solid at temperatures of 4000 - 6000° abs. Uranium melts at T = 1150° abs. A more refractory substance, uranium oxide, melts at T = 2100° abs. Even graphite vaporizes at a temperature of about 4000° abs.

For these reasons, a design solution is desirable in which not all parts of the packet of active substance would be subjected to intense heating, and the colder parts would ensure the necessary mechanical strength of the packet as a whole. Another possibility in this case is to have a part of the active substance melt and vaporize during operation.

It must, in general, be noted that the reserve of active substance is in no way determined by the scanty quantities given in Table IV.8, calculated on the basis of the energy balance. This reserve is determined at least by the value of the critical mass. It can also be expected that the quantity of active substance will be still further increased, with the object of the securing the necessary heat-transfer surface.

Figure 4.4 shows a second possible system of utilizing atomic energy in a rocket engine.

The working medium is placed in the tank (1) and is fed by the pump (2) feeds to the engine. On passing through the control device (3), the cooling jacket (4), and the chamber head (5), the working medium in the atomized state, enters the engine chamber.

The active substance, in the form of a solution or suspension, is placed in the tank (9). The pump (8) forces the substance through the regulator (7) into the annular collector. From the collector the active substance is injected through the nozzle system (6) into the engine chamber. As a result of the nuclear reactions taking place in the chamber, the working medium is heated and then expands in the

nozzle. This system of utilizing atomic energy appears highly tempting, since it ensures optimum heat-transfer conditions in turbulent flow.

The primary difficulty in the realization of the second system is the unreasonably large size of the chamber. The value of the critical mass in this case is
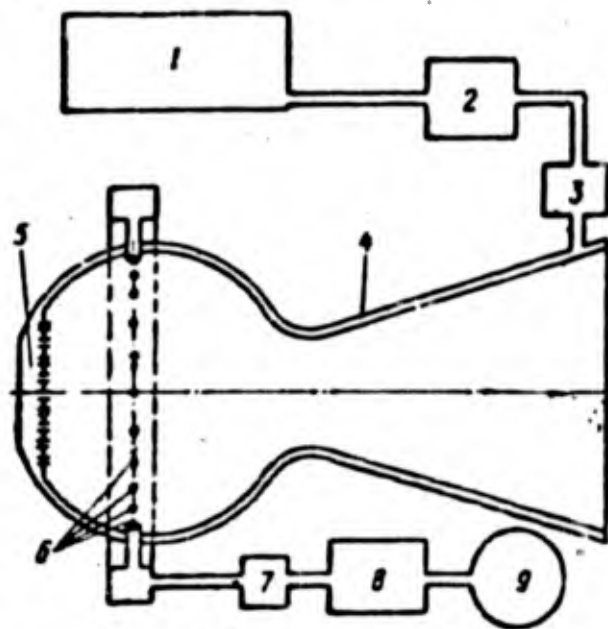
Fig.4.4 - Layout of Atomic Rocket Engine with Injection of
Active Substance into the Chamber

1 - Tank with liquid working medium; 2 - Pump for working medium;

3 - Instrument controlling feed of working medium; 4 - Cooling
jacket; 5 - Head with nozzles for injection of working medium;

6 - Zone of feeding solution of active substance (atomic fuel);

7 - Feed regulator; 8 - Pump feeding active substance; 9 - Tank
with solution of liquid active substance

replaced by the critical product of the pressure in the chamber p_{ch} and its radius R_{ch}. From certain calculations on the utilization of hydrogen as working medium, at a chamber temperature of 5000° abs, the necessary value of $p_{ch}R_{ch}$ is 12000 kg-m/cm^2. Thus, at a pressure of 100 kg/cm^2 in the chamber, the chamber must have a minimum diameter of 240 m. There is no use even in talking about the construction of chambers of such dimensions. Similar calculations for other working media give even

higher values for the critical size of the chamber.

Thermonuclear reactions, which are not dependent on the value of the critical mass, are known today. To excite such reactions, however, outside sources of high temperature are necessary. For the time being, the only such source is an atomic explosion which does not allow the utilization of thermonuclear reactions for the slow liberation of energy.

This short discussion of the possibilities of utilizing the energy of nuclear reactions in rocket engines will show that this problem is highly complex and that prolonged work still faces the scientist before the utilization of nuclear energy for a rocket engine becomes actually possible.

CHAPTER V

PROCESSES IN THE COMBUSTION CHAMBER OF A ROCKET ENGINE

1. Combustion in the Liquid-Fuel Rocket Engine

a. Preparatory Processes and Combustion in the Chamber of the Liquid-Fuel Rocket Engine

In the combustion chamber of a rocket engine, chemical combustion reactions take place, as a result of which the chemical energy of the fuel is converted into the thermal energy of the combustion product.

There are many proofs for the fact that the fuel components, before entering into reaction, must be vaporized and that combustion thus proceeds in the gas phase. At the same time, there are also examples of reactions in the liquid phase as in the case of the combustion of self-igniting fuels. It may be assumed, however, that in this case, the larger part of the fuel enters into reaction only after vaporization.

Thus or otherwise, the progress of a chemical reaction is possible only on contact between the molecules of combustible and oxidizer in the proportion necessary for combustion. For this reason, in order to effect the combustion of liquid fuels, it is necessary first to form as uniform a mixture as possible of the vapor of the combustible and oxidizer so that, at any point of the chamber, the oxidizer-combustible ratio is as close as possible to the ratio selected for the engine as a whole. The process of forming such a mixture is called mixture formation. The engine head is the organ for mixture formation.

The engine head contains nozzles for injecting the fuel and oxidizer into the chamber in a finely atomized form. The mixing of the fuel components may be started in the liquid phase by coalescence of the droplets and mutual dissolution of the combustible and oxidizer, but the principal portion of the mixture is formed after vaporization of the droplets and thorough mixing of the component vapors.

Vaporization and mixing of the components is connected with the phenomenon of the transfer of particles from one point of the chamber to another, i.e., with diffusional and convective flow in the combustion chamber. In addition, for vaporization and subsequent heating of the vapor to a temperature at which the chemical combustion reactions can begin and proceed, heat must be brought from the hotter zones of the chamber. The processes of transfer of particles and transfer of heat take place at one and the same time and are closely interrelated.

The laws of mechanical and thermal motion obeyed by the process of mixture formation are extremely complex. For this reason, in discussing mixture formation, we will confine the discussion to several qualitative conclusions.

It is obvious that, in designing an engine, it is of importance to have the head and the nozzles arranged in such a manner as to ensure the most uniform distribution of the fuel throughout the interior of the chamber.

Naturally, it will be easier to obtain a uniform mixture, the smaller the droplets of injected fuel, the more uniform the distribution of the droplets in the flare of the nozzle, and the more nozzles with a small discharge are located on the head. The size of the droplets and the uniformity of their distribution is determined primarily by the type of nozzle.

Two types of nozzle are used in liquid-fuel rocket engines: jet and centrifugal.

Jet nozzles (Fig.5.1) consist of a simple cylindrical opening of small diameter, allowing the afflux of a fine jet of liquid. The jet breaks down into droplets, as a result of the friction of the liquid and the gas in the chamber.

For a jet nozzle, a narrow and long jet of fuel is characteristic; the injec-

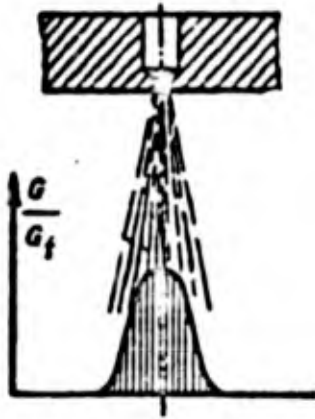tion begins rather far from the nozzle. The mass of the droplets along the cross section of the jet is irregularly distributed. The principal mass is located at the axis of the jet (cf.Fig.5.1). To eliminate this disadvantage, jet nozzles are placed in such a way that, at one point of the chamber, two or more jets flowing from different nozzles intersect (Fig.5.2). In this case the design is often so arranged that the jets of fuel and oxidizer meet at that point of intersection. As a result of the collision of the jets, they are broken down more rapidly into droplets, thus improving the mixing of the fuel components.

Fig.5.1 - Jet Nozzle and the Law of Mass Distribution of Drops along the Cross Section of the Nozzle Flare

Centrifugal nozzles (Fig.5.3) give better atomization. In these nozzles, the fuel passing through the nozzle channel is given a rotary motion, which is preserved even after leaving the channel. Under the action of the centrifugal forces, the emerging jet contracts into a film which is rapidly broken down into droplets.

The flare of centrifugal nozzles is wide and short, and the drops are distributed more uniformly in it, although the maximum concentration of fuel is obtained over a circle of a certain radius described around the axis of the nozzle.

Fig.5.2 - Jet Nozzles with Intersecting Axes

The liquid is given a rotary motion in the channel of a centrifugal nozzle, either because of its tangential admission to the nozzle (cf.Fig.5.3) or as a result of motion along a helical channel formed by the threaded insert (worm) and the wall of the nozzle.

Sometimes centrifugal and jet nozzles are used simultaneously in engine heads.

The discharge of the components through the nozzle is determined by their inside cross section and by the pressure drop at the nozzles; in this case, the discharge is proportional to the square root of the pressure head. The greater the head, the higher the quality of fuel atomization. On the other hand, an increase in the pressure drop leads to a rise in the necessary feed pressure, which results, especially under forced feed, in an increase in engine weight.
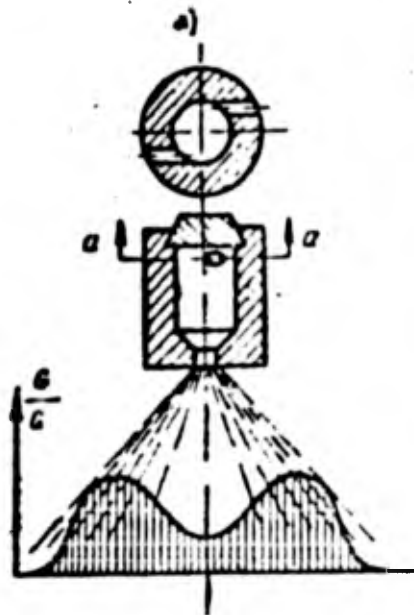
As stated above, the procurement of a uniform mixture depends on using a large number of nozzles with a small discharge through each nozzle.

In fact, engines built so far have a large number of small nozzles. For example, in the V-2 rocket engine, the fuel was injected at the rate of about 3 kg/sec into a single precombustion through 68 nozzles (44 of which were of the centrifugal and 24 of the jet type) so that a discharge of only 42 gm/sec falls to the share of one nozzle.

Fig.5.3 - Centrifugal Nozzle and Law of Mass Distribution of the Fuel Along and Over the Cross Section of the Nozzle Flare

a) Section through a - a

To obtain the most uniform possible distribution of the components in cross section, the nozzles for the combustible and oxidizer are arranged in a definite order over the head. The main and uniform distribution of combustible and oxidizer may be disturbed on the periphery of the head. Here only several fuel nozzles are often installed in order to form a vapor film next to the wall to protect the wall from charring.

The heat necessary for vaporizing and heating the fuel vapor is transferred to the droplets in three ways: because of the vortical motion of the gas in the head, by radiation from the interior of the gas at a high temperature; by radiation from

the hot walls of the engine; and, finally, after the beginning of the combustion reaction, directly by the heat liberated during the reaction. The vortical motion of the gas around the head is at its highest value in the transfer of heat to the fuel droplets during vaporization. This same vorti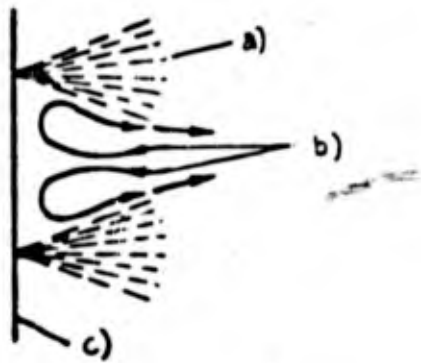cal motion favors the mixing of a volatile fuel. The vortical motion of the gas around the head is accompanied by reverse flow in the space between the fuel jets (Fig.5.4). These reverse currents entrain the heat necessary for vaporizing the fuel and encourage the mixing of the combustible and oxidizer.

Fig.5.4 - Diagram of Appearance of
Vortical Motion Near the Head
a) Fuel jet; b) Reverse currents;
c) Engine head

In a mixture of combustible and oxidizer vapors, chemical reactions start on continued heating; as a result heat sufficient for a further reaction over the entire volume of the combustion chamber is liberated.

In accordance with this picture of the combustion process in a liquid-fuel jet engine, the latter may be arbitrarily divided into several characteristic zones (Fig.5.5).

In the first zone, in immediate contact with the surface of the head, the fuel jets are atomized into droplets. For this reason, the zone may be termed the atomization zone. The other processes, namely, vaporizing and mixing, proceed at very low intensity in this system.

With further advance of the fuel along the chamber, vaporization becomes more and more intense, and mixing begins. In this zone, chemical reactions are also initiated, but their velocity is low because of the low temperature. Consequently, the second zone may be arbitrarily termed the zone of vaporization and displacement.

Finally, with increasing supply of the mixture (in the gas phase) and its

increasing temperature, intense chemical reactions begin to take place in the subsequent, or third, zone. In the first part of this zone, the rate of the chemical
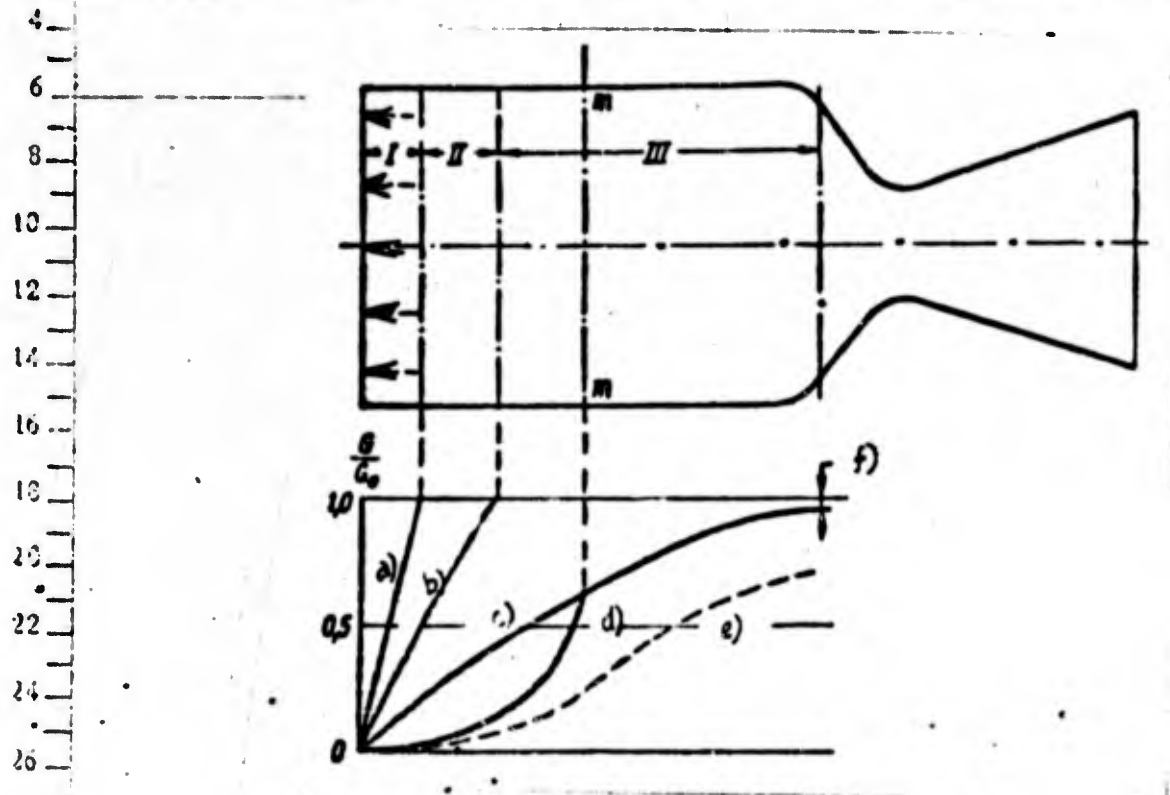
Fig.5.5 - Head of Combustion Chamber, and Division of the

Chamber into Zones

I - Zone of atomization; II - Zone of vaporization; III- Zone of mixing and chemical reactions; m-m - Cross section of transition of combustion from the kinetic zone to the diffusion zone

a) Injection; b) Vaporization; c) Mixing; d) Chemical reactions;

e) Temperature; f) Physically incompletely burned fuel

reactions is still low so that the combustion of the fuel determines the velocity or, as it is also called, the kinetics of the chemical reactions. This region of the combustion chamber is called the zone of kinetic combustion.

The temperature rise leads to a sharp rise in the chemical reaction velocity and, beginning at a certain temperature value, all of the mixed fuel undergoes practically instantaneous combustion. The rate of combustion will almost completely depend on the rate of mixing of the components. Since the rate of mixing is deter-

mined by the rate of diffusion*, this region is called the zone of diffusional combustion. The combustion process in a liquid-fuel rocket engine takes place mainly in the diffusion zone, so that the time necessary for combustion is determined by the rate of mixing. Thus the third zone in the combustion chamber is the zone of mixing and chemical reactions.

Residence Time of Fuel in the Combustion Chamber

The dimensions of the combustion chamber must be such that the mixing and chemical reactions are able to proceed to completion before exit into the engine nozzle. This ensures the most complete conversion of chemical energy into thermal energy and reduces the physically incomplete combustion.

The necessary dimensions of the chamber are determined from the nominal value of the residence τ of the fuel in the chamber.

If the fuel consumption, the temperature of the combustion product at the end of the chamber, and the pressure are denoted by G, T_k, and p_k, respectively, then the total volume of gas passing through the chamber in unit time is

$$V = G\frac{RT_\kappa}{p_\kappa}.$$

This volume of gas will remain in the chamber during the period of time

$$\tau = \frac{V_\kappa}{V} = \frac{V_\kappa p_\kappa}{GRT_\kappa},$$

where V_k is the volume of the combustion chamber.

The quantity τ is termed the residence time.

The value of τ only indirectly reflects the actual residence time of the fuel and its combustion products in the chamber. It is a fact that the volume of a part

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* What is meant here is the so-called turbulent diffusion, whose essential nature does not consist in the motion of the individual molecules, but in the disordered mixing of small volumes of gas.

of the combustible as it undergoes combustion in the chamber increases from the negligibly small volume of liquid fuel to the value V_k, while the residence time is calculated exactly from this maximum volume. Thus the actual residence of the fuel in the chamber is longer than the value of τ but bears a definite relation to it.

The residence time τ necessary for a sufficiently complete combustion of the fuel is determined experimentally as well as on the basis of studies of engine designs. In existing engines, this amounts to 0.003 - 0.008 sec. With increasing pressure, the residence time in the chamber increases, meaning that a chamber with the same fuel discharge at higher pressure can be made smaller.

The residence time in the chamber for a given design of the head is the principal factor determining the physical completeness of fuel combustion, i.e., that portion of the fuel which has time to enter into chemical reaction in the chamber.

Design of Combustion Chambers and Engine Heads

As will be seen from eq.(5.1), the residence time τ does not depend on the shape of the combustion chamber so that, for a given volume, the chamber may have any desired shape. The choice of the shape of the combustion chamber, however, cannot be entirely arbitrary. With a long chamber of small cross section, the necessary number of nozzles cannot be placed on the head. With a short chamber, the zone of mixture formation occupies a considerable part of the volume of the chamber, and the length of the mixing and combustion zone becomes very short. The normal ratio of the cross-sectional area of a chamber to the area of the critical cross section ranges from 3 to 10.

It should be noted that the necessary volume of the combustion chamber depends on the operational quality of the head. The more uniform the fuel mixture supplied by the head, the smaller can be the volume of the combustion chamber. Moreover, to reduce the necessary chamber volume, the head should distribute the fuel mixture over the cross section of the chamber in such a way that the fuel reaches all parts of the

chamber and that the combustion process takes place uniformly over the cross section of the chamber. In other words, the shape of the combustion chamber and the shape of the head must be closely interrelated.

In modern engines, combustion chambers of two geometric forms are most often used: cylindrical and spherical (or close to spherical).

An advantage of the spherical chamber is the fact that this chamber, for the same volume, will have a smaller surface area than a chamber of any other shape. The small surface area of the chamber is responsible for its low weight and the small amount of heat that will be transferred to the cooling system.

A spherical chamber is also advantageous in its mechanical strength indices. At equal strength, the wall of a spherical chamber is only half as thick as the walls of a cylindrical chamber. For this reason, if the thickness of the chamber walls is not determined by technological or operating considerations but by strength characteristics (this is the case in large engines and in engines with a high pressure p_k in the chamber), the spherical shape of the chamber should be given preference.

A disadvantage of the spherical chamber is the complexity of its manufacture and the difficulties connected with obtaining good operation of the head and good operation of the chamber at one and the same time. In this respect a cylindrical chamber has greater advantages.

A study of Fig.5.6 which shows the chamber of a liquid-fuel rocket engine booster, indicates that the flat head installed on this engine allows a uniform distribution of the fuel over the cross section of the chamber, with no zones not reached by the fuel and no zones without combustion (so-called "dark" zones).

Such a flat head, when installed on a pear-shaped engine (Fig.5.7) does not permit complete utilization of the chamber volume for combustion. The portion of the chamber beyond the limits of the cylindrical part, with a diameter equal to the diameter of the head, is practically unutilized for fuel combustion. In addition, the size of the flat head does not permit installation of a large number of centrif-
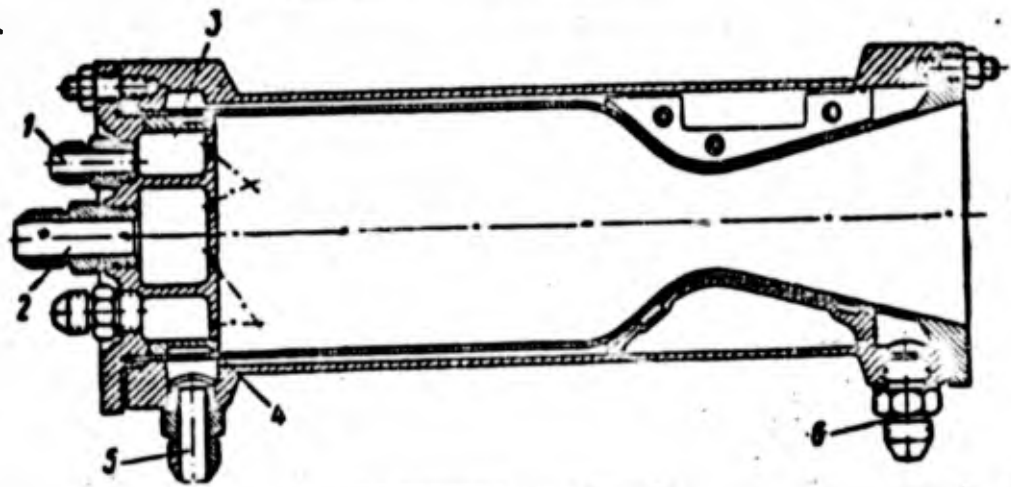
Fig.5.6 - Cylindrical Chamber of Liquid-Fuel Rocket Engine Booster

1 - Combustible supply; 2 - Oxidizer supply; 3 - Fuel port for internal cooling; 4 - Gap for outlet of internal cooling fuel; 5 - Oxidizer supply for cooling combustible; 6 - Outlet of oxidizer from cooling jacket
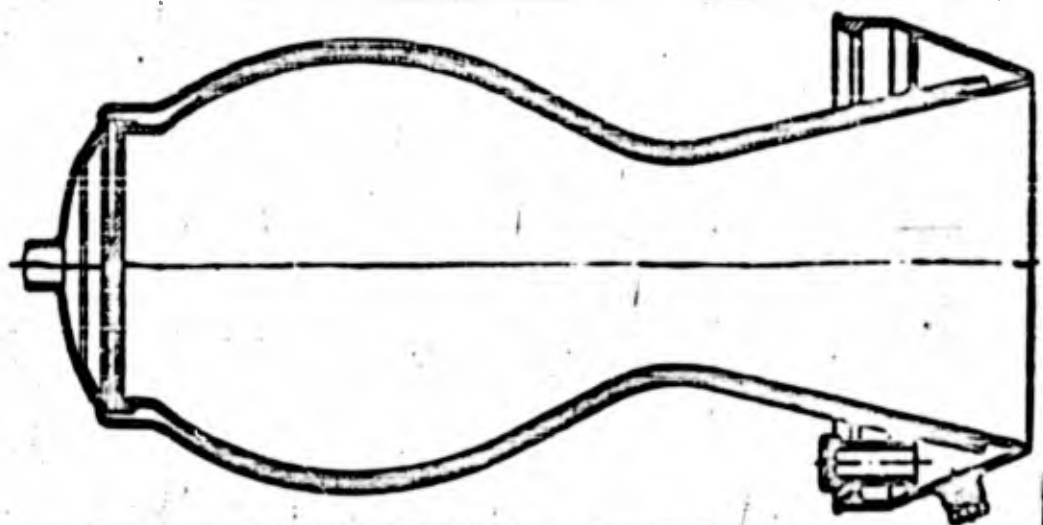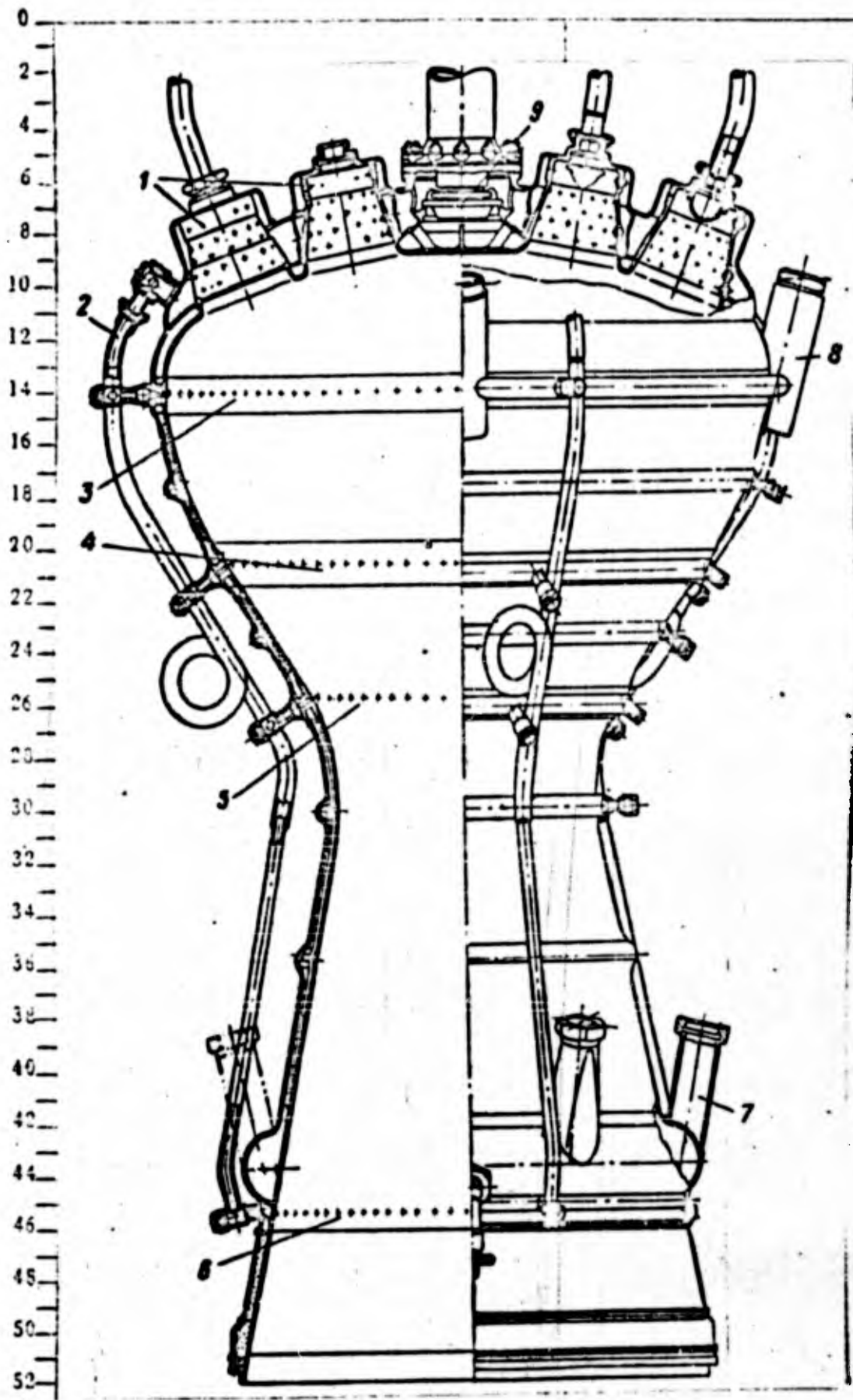

Fig.5.7 - Pear-Shaped Chamber with Flat Head

Fig.5.8 - Chamber of Engine of Long-Range V-2 Rocket

1 - Precombustion chambers; 2 - Feed pipes for internal cooling fuel; 3,4,5,6 - Zones of intake ports for fuel to inner surface of chamber wall; 7 - Pipes supplying fuel to cooling jacket; 8 - Brackets attaching engine to frame; 9 - Main alcohol valve

ugal nozzles. In this engine, the inferior jet nozzles had to be used.

The combustion-chamber volume in the engine of the V-2 rocket (Fig.5.8), with 18 precombustion chambers installed on its head, is utilized just as incompletely. The mixture, prepared in the precombustion chambers, is discharged in a heavy jet into the chamber; although these jets, on colliding, are intensely mixed, a considerable part of the chamber volume included between the jets discharged from the precombustion chambers, is not utilized for the combustion process.

Figure 5.9 gives an idea of the layout of the flat head with jet nozzles.
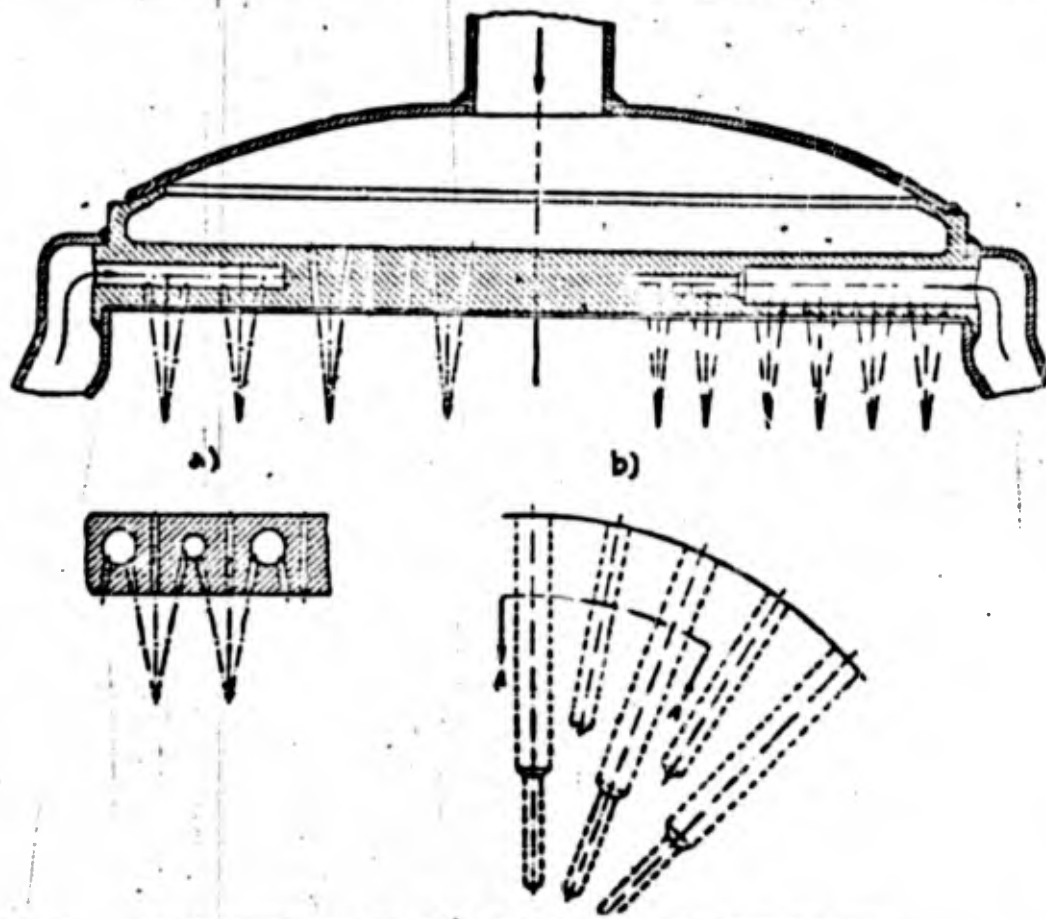
Fig.5.9 - Flat Head

a) Section through A-A; b) Arrangement of radial openings for oxidizer feed

This head is provided with 432 combustible nozzles 1.5 mm in diameter and 324 oxidizer nozzles 2.6 mm in diameter. The combustible and oxidizer ports, as shown by the cross section of the head and the section through A-A, are drilled obliquely

at an angle to each other, to ensure good atomization of the jets on contact and to initiate mixture formation in the liquid phase. The combustible is fed from the upper cavity of the head, while for the supply of oxidizer long radial openings must be drilled, which must not intersect the fuel ports. The manufacture of such a head is highly complicated.

Centrifugal nozzles may also be placed on a flat head. It can be assumed that they are able to yield a more uniform distribution of the mixture over the cross section of the chamber. In addition, centrifugal nozzles ensure intersection of the
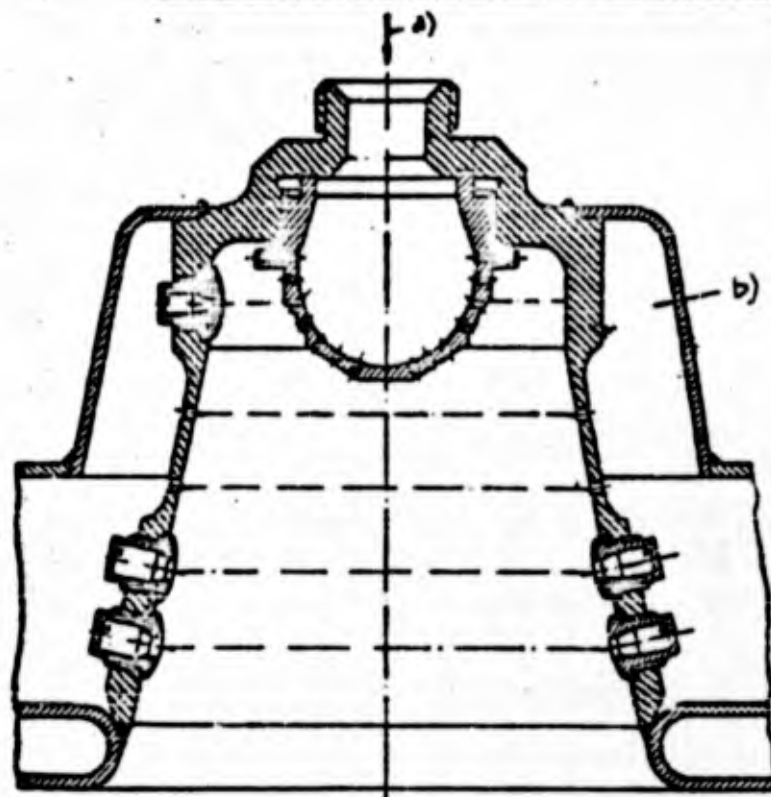
Fig.5.10 - Precombustion Chamber of Engine in Long-Range V-2 Rocket

a) Oxygen supply; b) Alcohol cavity

combustible and oxidizer jets in the standard arrangement of the nozzles, in which their axes are parallel to the axis of the chamber; in this way, the installation of centrifugal nozzles does not demand the drilling of slanted openings. Centrifugal nozzles, however, occupy a larger space so that the head must be larger. In a cylindrical chamber this is readily possible, without increasing the chamber volume, by

increasing its diameter and decreasing its length.

In the spherical combustion chamber, due to conditions of assembly, it is very difficult to install the nozzles directly on its bottom. In addition, the small bottom area makes it difficult to accommodate the necessary number of small nozzles. For this reason, precombustion chambers are used in engines with spherical chambers (Fig.5.10). Into each such chamber the oxidizer is injected through one nozzle with a large number of holes. The combustible is supplied through nozzles located on the lateral conical surface of the precombustion chamber. It is obvious that such a system of mixing does not allow uniform distribution of the components over the cross section of the precombustion chamber (at least not by simple means).

To improve the mixture formation, a complex system of coordinated nozzles is used in the above described precombustion chamber. The oxygen is injected through ports placed along concentric circles and inclined to the axis of the antechamber at various angles, in order to fill the interior of the chamber as uniformly as possible with the oxidizer jets.

The zones of nozzles for the combustible are arranged to correspond to the zones of the oxidizer ports. The upper zone contains centrifugal nozzles. The small flare of these nozzles protects the walls of the antechamber from direct contact with oxygen. The next two zones consist of jet nozzles which, because of the greater range, direct the fuel to the center of the precombustion chamber. In the lower zones, centrifugal nozzles are again installed. The above measures permit improvement of the quality of mixture formation, but as a whole this formation is still inferior to that in engines with a flat head. As a result, the relative volume and weight of the combustion chamber are increased.

Ignition of Fuel in the Liquid-Fuel Rocket Engine

The course of the steady combustion process in the engine has been described above. The initial inflammation of the liquid fuel in the combustion chamber, or

ignition, makes special demands on the engine in some cases.

As we already know, fuel may be self-igniting or non-self-igniting. The conditions of its ignition in the combustion chamber vary. Non-self-igniting fuels are ignited by their injection into the primer jet which fills the combustion chamber. The primer jet is made heavy enough to ignite the main components as they are fed during the starting process. Non-self-igniting fuels make no particular demands on the design of the head. Self-igniting fuels begin to react and liberate heat when they come into contact with each other, still in the liquid state. For this reason it is advisable, in order to ensure reliable ignition, to provide good contact for the components in the liquid phase.

According to some data, it is more expedient to use jet nozzles with intersecting axes for self-igniting fuels.

Self-igniting fuels have a certain autoignition lag. On starting the engine, unburned liquid fuel accumulates in the chamber. The subsequent combustion of the accumulated fuel leads to a sharp rise in pressure ("surge"), which may be harmful to the engine.

To reduce the accumulation of fuel in the chamber, the fuel discharge must be artificially reduced during the initial stage of starting.

For this reason, systems of engine feed with self-igniting components or engines with chemical ignition use devices ensuring a slow increase in fuel supply during the starting period. These devices are either in the form of throttle valves, which open slowly during starting (see description of the engine for the Zenith rocket) or in the form of rotating valves in the engine head, which gradually permit access of fuel to the nozzles.

Oscillatory Combustion

In stand tests and operation of liquid-fuel rocket engines, it has been noted that so-called oscillatory burning may occur in the combustion chamber. This consists

in a periodic variation in gas pressure, with a frequency up to 200 cps (Fig.5.11). The amplitude of the pressure oscillations may reach such high values as to threaten potential destruction of the engine.
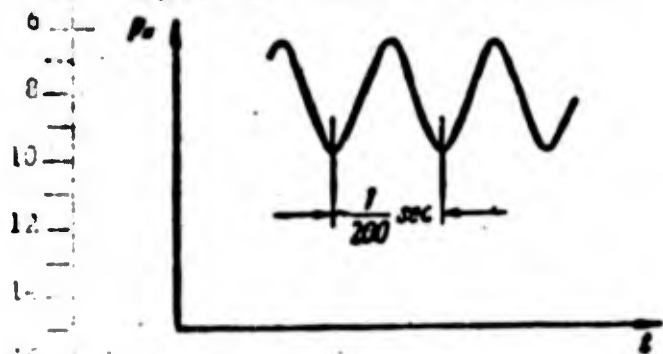

Fig.5.11 - Pressure Variation in Chamber during Oscillatory Combustion

The physical picture of the occurrence of oscillatory combustion is not entirely clear, but a certain qualitative explanation can be given.

Assume that the pressure in the feed system, for example in the engine tanks or forced feed, remains constant. Assume further that, for some reason, the pressure in the combustion chamber has dropped below its rated value. In that case, the amount of fuel discharged through the nozzles will increase since the pressure drop at the nozzles will rise. Such increased fuel discharge through the nozzles will continue until the first portion of the fuel at increased discharge rate, after a time of the order of τ, is converted into gas and begins to leave the engine. From this moment, the pressure in the chamber of the liquid-fuel rocket engine rises proportionally to the increasing rate of discharge per second of the combustion products of the fuel through the critical cross section (see later in text) and becomes greater than the rated pressure. In this connection, the pressure drop at the nozzles as well as the discharge of fuel through these nozzles decrease. After the time of the order of τ, the discharge of the gaseous products likewise decreases, causing the pressure in the chamber to drop thus restoring the conditions for repetition of the preceding cycle of oscillations.

The magnitude of the oscillations of discharge at constant initial disturbance of the pressure in the chamber depends on the rated pressure drop at the nozzles. The greater this pressure drop, the smaller will be the relative variation in pressure drop at the nozzles and the smaller will be the variation in discharge. Thus,

the increase in the pressure drop at the nozzles counteracts the appearance of pressure fluctuations and of oscillatory combustion.

The volume of the combustion chamber influences the generation of oscillations in exactly the same way. The greater the volume of the chamber, the larger will be the portion of excess fuel discharge expended on changing the supply of gas to the chamber. Consequently, pressure fluctuations are attenuated in a large chamber.

Pressure fluctuations in the chamber may also cause oscillation of the fuel column in the feed tubes; at certain frequency ratios, this may lead to an increase in the amplitudes of oscillatory combustion. In cases where, during oscillatory combustion, the pressure fluctuations are so great that the arrival of fuel in the chamber is completely stopped at a given moment, an explosion of the engine is entirely possible when the fuel feed is subsequently resumed.

Besides an increase in the pressure drop at the nozzles, other measures to prevent oscillatory combustion are: increasing the rate of combustion which shortens the time necessary for conversion of the fuel into gaseous products, and selecting such geometric dimensions of the chamber and feed system as will not permit generation of oscillations.

2. The Burning of Rocket Powders

Combustion Rate of Powder

Rocket powder is a uniform gas-impermeable mass, where each small volume contains the necessary mixture of combustible and oxidizer elements. The burning of powder takes place from the surface, with the flame front penetrating into the interior of the body, meaning that the arching of the powder takes place only as the overlying layers are burned away.

It has been theoretically and experimentally established that the burning of powder is preceded by a thermal decomposition of the substance on its solid surface. The intensity of the decomposition is determined primarily by the rate of heat

transfer from the zone where further combustion of the gaseous decomposition products, formed on the surface of the burning powder, takes place. The heat is transferred to the surface by thermal conduction and radiation, since the flow of the
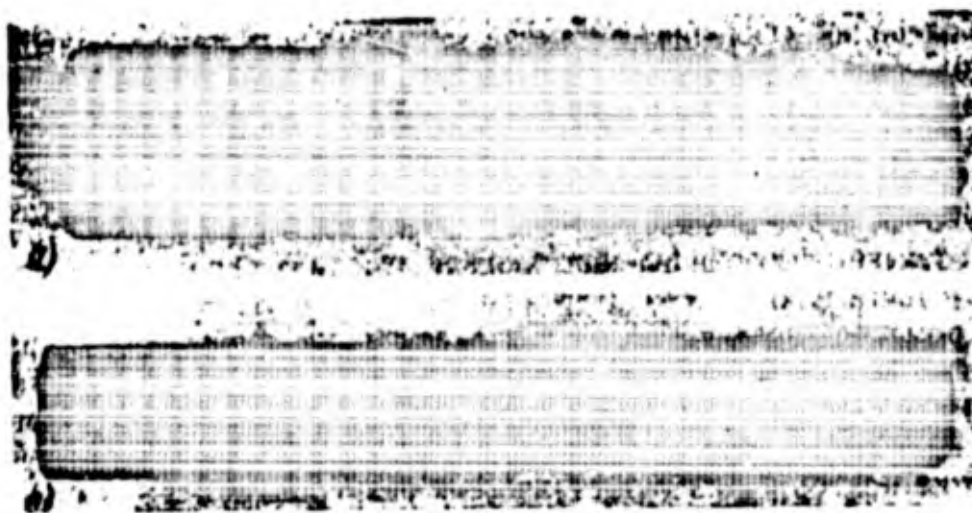

Fig.5.12 - Appearance of Powder Grain before Start of Burning (a)

and 70% Burned (b)

gaseous products is always directed away from the burning surface so that heat transfer to the powder grain by convection is impossible.

The value of the combustion rate u_p, i.e., the thickness of the layer of powder burned away in unit time, is taken as the basic characteristic of the burning of powder. This quantity is usually expressed in cm/sec.

Since powder is a uniform mass, it is natural to expect uniform burning of the powder over its entire burning surface. Actually, experiments with sudden stopping of the combustion of a powder grain have confirmed this assumption.

Figure 5.12a shows the appearance of a powder grain before burning. This grain was ignited over its entire surface and then was extinguished after a certain time (Fig.5.12b). It will be seen from the photographs of the grain that burning proceeds rather uniformly over the entire surface.

The weight of powder burned in unit time and, consequently, the quantity of combustion products formed is

$$G_\rho = F_\rho u_\rho \gamma_\rho. \qquad (5.2)$$

where F_p is the burning surface of the powder grain;

   u_p is the burning rate of the powder;

   γ_p is the specific gravity of the powder.

Since the specific gravity of the powder is a constant ($\gamma_p = 1.6 - 1.7$ kg/ltr), the quantity of gases formed depends on the size of the burning surface and the rate of burning.

The burning rate of powder is primarily determined by the pressure under which burning takes place. An increase in pressure facilitates the supply of heat to the powder grain and accelerates the reactions taking place on its surface.

At pressures up to 200 kg/cm^2, which are characteristic for the combustion chambers of powder engines and of powder pressure accumulators, the dependence of the burning rate of powder on the pressure p may be approximately represented by the empirical formulas:

$$u_p = \alpha + \beta p \qquad (5.3)$$

and

$$u_p = b p^n. \qquad (5.4)$$

where α, β, b, and n are experimental constants.

The value of the exponent n in eq.(5.4) varies from 0.6 to 0.8. The coefficients α, β and b depend not only on the composition of the powder but also, to a considerable extent, on the initial temperature of the powder (before burning begins).

The initial temperature of the powder, naturally enough, has an influence on the rate of burning: an increase in this temperature facilitates the progress of the reaction on the surface of the charge and increases the burning rate. At the same time, owing to the relatively high burning rate and the low thermal conductivity, the entire powder grain is not heated through during the process of burning, so that

the temperature of the powder remains constant (only a very thin layer, practically reacted, is heated through).

The dependence of the burning rate of a powder charge on its initial temperature
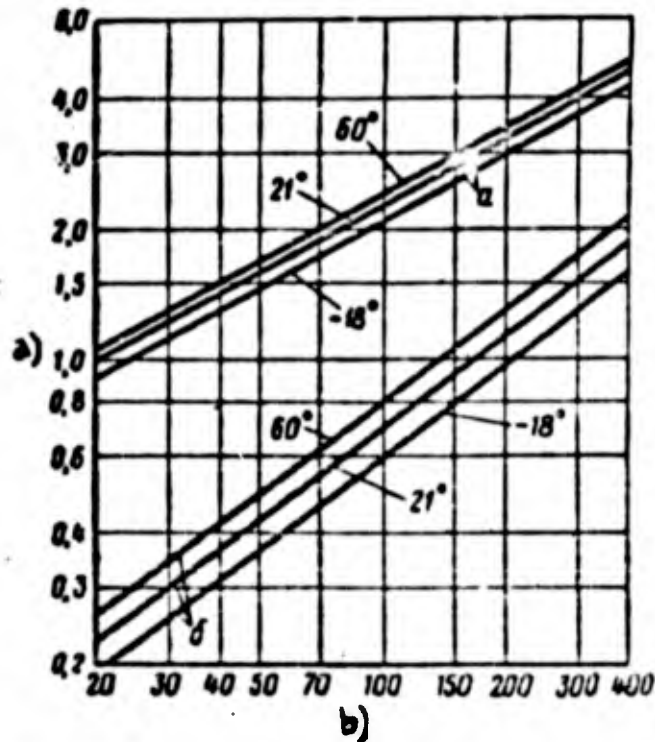

Fig.5.13 - Pressure and Temperature Dependence of the

Burning Rate of Powder

a - Fast-burning powder; b - Slow-burning powder

a) Burning rate, in cm/sec; b) Pressure, in kg/cm²

is rather clearly perceptible and is the cause of a considerable variation in the weight discharge of the combustion products over the temperature range from -50° to +50°C, characteristic for different seasons and different climatic conditions.

Figure 5.13 shows typical pressure and temperature dependences of the burning rate of powders, plotted on a logarithmic scale.

The upper group of straight lines refers to a powder with a high burning rate (2 cm/sec at a pressure of 80 kg/cm² and an initial temperature of t = 21°C for the charge). The burning rate of this powder, however, is only slightly pressure-dependent (n = 0.52). The influence of the initial temperature is likewise slight.

The lower group of straight lines refers to a slow-burning powder (burning rate, 0.6 cm/sec at the same pressure and temperature). However, for this powder the temperature dependence of the burning rate, and particularly its pressure dependence, are stronger (n = 0.71).

Shape of Rocket Powder Charges

The quantity of gas formed in unit time under constant pressure is determined, as follows from eq.(5.2), by the size of the burning surface of the charge F_p. During the process of burning of a powder grain, the value of F_p generally does not remain constant and may either decrease or increase. If the area F_p decreases during the burning process, the quantity of gas formed in unit time also decreases. Such burning of a charge is called regressive. If the burning surface increases with time, then the quantity of gases formed in unit time likewise increases. The burning of the charge in this case is called progressive.

By giving a powder grain different shapes, the law of formation of gases with time may be regulated within certain limits.

In designing powder rockets, constant engine thrust over the entire trajectory is usually attempted. For this it is obviously necessary to obtain a constant quantity of gases in unit time, i.e., to have a constant burning surface of the powder grains. To satisfy this condition, the grains are given special shapes. As an example, we may mention the hollow cylindrical grain, known also as tubular grain, shown in Fig.5.14. In this grain, the burning away of the outer cylindrical surface leads to a decrease in the area of the burning surface,

Fig.5.14 - Burning of a Tubular Grain

The broken line shows the surface of burning after t sec. The area burning away from the surface is hatched

while the burning away of the inner surface leads to the same increase in the area of the burning surface. Thus the size of the burning surface varies only by reason
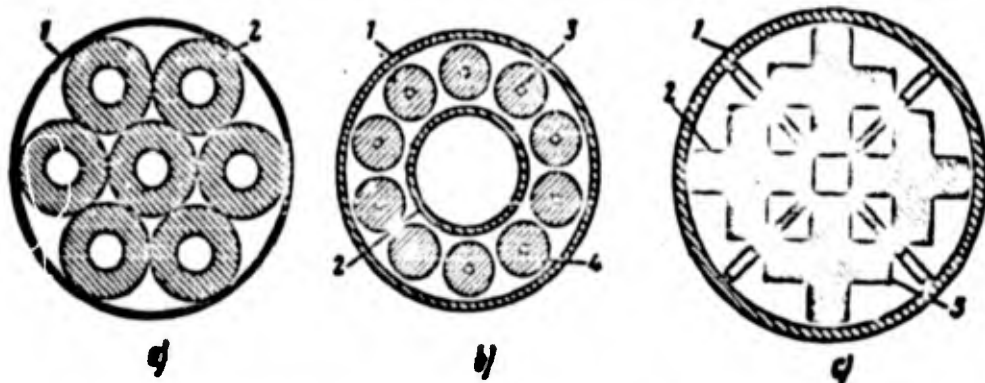

Fig.5.15 – Shapes of Powder Grains of a Rocket Charge

a – Seven-grain thin-arch charge: 1 – Wall of chamber; 2 – Powder grain;

b – Charge of tubular grains held in place by rods: 1 – Wall of rocket chamber;

2 – Center column for explosive charge; 3 – Rod for holding grain; 4 – Powder grain;

c – Charge of cruciform grains: 1 – Wall of rocket chamber; 2 – Cruciform powder

grain; 3 – Steel partitions

of the decrease in the surface area of the burning faces of the grain. If the grain is very long, the influence of the faces on the total burning surface is very small,

Fig.5.16 – Armored Grain

a) Armored coating; b) Burning surface

and the burning surface may be considered to be practically constant. The burning will be "weakly regressive".

We note that in some cases, for instance to obtain a high rocket speed on launching from short guide rails, rapid combustion of the powder (in 0.1 – 0.3 sec) is necessary. In such cases the surface of the grains is increased and their thickness decreased (the thickness of the arc is decreased). The charge used is of the multi-grain type (Fig.5.15a). Other more complex shapes of grains are also used, providing for the necessary law of variation of the burning

surface (cf. Fig.5.15b and c).

In special cases a charge with a small burning surface, but one which will burn for a long time (tens of seconds) may be needed. This is necessary, for instance, for powder pressure accumulators. To slow down the burning, so-called armored grains are used. In these grains, part of the powder surface is covered with a plastic (for example, acetyl cellulose); which does not itself burn and prevents the surface of the grain covered by it from taking fire. Figure 5.16 shows a grain armored on all sides except one face.

Burning of the Powder Charge in the Chamber of a Powder Engine

The above relationships are characteristic for the burning of a powder charge in the absence of gas motion along the surface of the grain. When the grain burns
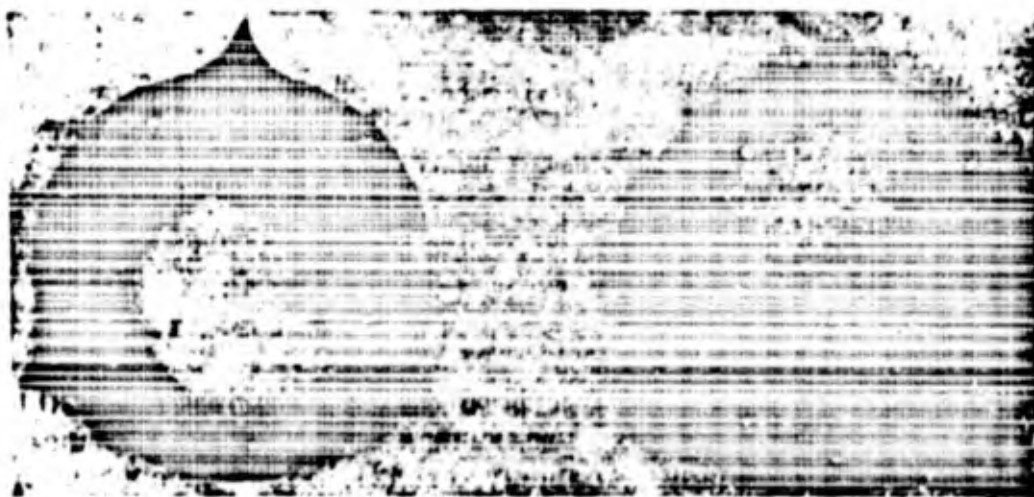
Fig.5.17 - Partially Burned Powder Grain. Left - view from the bottom of the chamber; right - view from the nozzle

in the chamber of a powder engine, however, the gases formed flow along the surface of the grain in their motion toward the nozzle. Experience shows that the burning rate of powder depends on the velocity of the flow washing it: the higher the velocity of this flow, the higher will be the burning rate. This is explained by the increase in heat supplied from the burning gases to the powder.

In powder engines, the degree of filling of the combustion chamber by fuel is

made as great as possible. The space between the burning grains is small, and the velocity of the gases washing the surf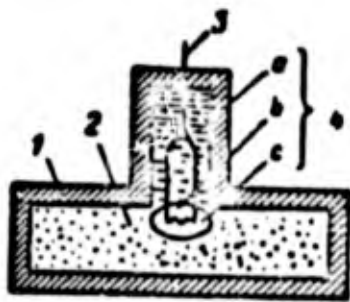ace of the grains is rather considerable. The velocity of the gases increases in the direction toward the exhaust. For this reason, the powder grains burn more rapidly toward the nozzle. Figure 5.17 shows a photograph of a grain that has partically burned in the engine. It is clearly shown that more of the powder grain has burned away on the side of the nozzle.

At low pressures in the engine combustion chamber, intermittent or so-called anomalous burning is possible. This consists in a periodic extinction and reignition of the powder charge. The pressure under which anomalous burning takes place depends on the composition of the powder and on the temperature of the charge. A decrease in the initial temperature of the charge favors the appearance of anomalous burning. For rocket powders, anomalous burning appears at pressures of 20 - 40 kg/cm^2.

Ignition of the Rocket Powder Charge

A rocket powder charge is ignited by an igniter.

Figure 5.18 gives a schematic diagram of the layout of the igniter.

For ignition of the igniter, an electric current is supplied across the wires of the ignition device (4), set in the mastic seal (a), to the incandescent filament (b) which, on becoming heated to incandescence, lights the readily ignitable composition (c). This composition then ignites the charge (2).

The igniter box (1) may be made of plastic or metal.

The hot gases formed by the ignite wash the surface of the main powder charge

Fig.5.18 - Layout of Igniter

1 - Case of igniter; 2 - Charge of igniter; 3 - Wires bringing current to the electric detonator; 4 - Electric detonator: a - Mastic seal; b - Incandescent filament; c - Inflammable composition

and ignite it. During the process of ignition, the temperature of the charge sur-
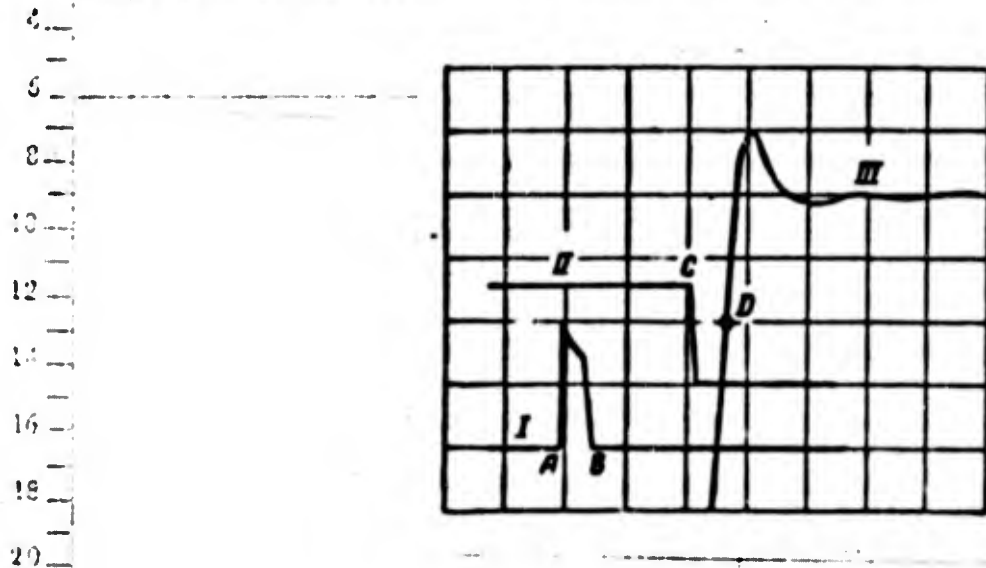face is first increased to the ignition point, and then the pressure in the chamber

Fig.5.19 — Course of Ignition with Time

I — Curve of current strength in incandescent filament circuit;

A — Current supply to incandescent filament; B — Lighting of
incandescent filament;

II — Curve of internal stresses the casing; C — Beginning of
rupture of the casing;

III — Curve of pressure build-up in combustion chamber; D — Pressure
sufficient to initiate burning of charge

is increased to a level ensuring normal burning of the charge.

The ignition time of a powder charge must be as short as possible. This
requires intense heat transfer from the combustion products of the igniter to the
powder charge.

Under the conditions of ignition, when the velocity of the gases in the chamber
is low, heat transfer by radiation is of great importance for the heat transfer.
But the radiative power of gases is low. To increase it, the igniter charge is so
compounded that its combustion products contain a considerable number of solid par-
ticles which intensely radiate heat. For this reason, the igniter charge is made

either of black powder (smoky powder), which yields a certain number of solid particles, or of a mixture of magnesium (or aluminum) powder and potassium chlorate ($KClO_4$).

More rapid ignition (5 - 10 millisec) is provided by igniters of $KClO_4$ and Mg (or Al). They are more dangerous to handle, however. In addition, the metal powder in their composition may oxidize on prolonged storage, which will lead to failure of the igniter. The ignition time of a black-powder rocket charge is longer (25 - 30 millisec), but such an igniter is more reliable after storage.

Figure 5.19 shows the development of the ignition process with time.

In the ignition chamber of a powder engine, the igniter is placed on the faces of the charge. An igniter located at the bottom of the chamber ensures more reliable ignition. In this case the igniting gases before being discharged through the nozzle, flow around the entire charge and heat it.

3. Combustion Products and their Properties

Parameters of State of the Gas Mixture

The combustion process in the combustion chamber of a rocket engine consists of a number of complex chemical reactions, together with the preparatory processes necessary for their realization.

The primary result of the combustion process is the conversion of the liquid or solid fuel into gaseous combustion products heated to a high temperature. Since the fuel always contains several elements, the combustion product consists of a mixture of various chemical compounds, for the most part gaseous. Let us consider the principal properties of the gaseous combustion products, and let us introduce the quantities that determine their state.

The state of a gas is characterized by the following parameters: absolute pressure p, absolute temperature T, density ρ (or specific gravity γ), and also the gas constant R.

It is well known that for ideal gases (or for mixtures of ideal gases), the parameters p, ρ, and T are related by the equation of state (Clapeyron's formula)

$$\frac{p}{\rho} = gRT. \tag{5.5}$$

The density of a gas is connected with the specific volume by the relation

$$gp = \frac{1}{v}. \tag{5.6}$$

Consequently, the equation of state may be written as follows:

$$pv = RT. \tag{5.7}$$

The value of the gas constant for a mixture of gases is determined by its composition. For calculating R, the following relation can be used:

$$R = \frac{\bar{R}}{\mu_\Sigma}; \tag{5.8}$$

where $\bar{R}$ is the universal gas constant related to 1 kg-mole of any gas or any gas mixture; $\bar{R}$ = 848 kgm/kg-mole deg or, expressed in thermal units, $A\bar{R}$ = = 1.986 kcal/kg-mole deg;

μ_Σ is the apparent molecular weight of the mixture.

The apparent molecular weight of the mixture is

$$\mu_\Sigma = \sum \mu_i r_i. \tag{5.9}$$

where μ_i is the molecular weight of the ith gas forming the mixture;

r_i is the volumetric proportion of the gas, of molecular weight μ_i.

The volumetric proportions of the gases in the mixture are most simply expressed in terms of the partial pressures p_i.

As everyone knows, the partial pressure of a gas means the pressure that a gas would have if it occupied the entire volume occupied by the gas mixture. The total pressure of the gas mixture p_Σ is equal to the sum of the partial pressures:

$$p_\Sigma = \sum p_i.$$

The volumetric proportion of the gas in question here is

$$r_i = \frac{p_i}{p_z}. \tag{5.10}$$

Taking this relation into account, we get instead of eq.(5.9)

$$\mu_z = \frac{1}{p_z} \sum \mu_i p_i. \tag{5.11}$$

For a gas mixture of constant composition, the values of μ_Σ and R are constant; on the other hand, if the composition of the mixture varies, then the apparent molecular weight of the gas constant of a mixture will likewise vary.

Internal Energy and Heat Capacity of a Gas

One of the energetic characteristics of a gas is its internal energy. The internal energy represents the energy of motion of the gas molecules, and is usually regarded as the quantity of heat possessed by the gas. The energy of motion of a molecule is determined by the temperature of the gas and the structure of the molecule itself.
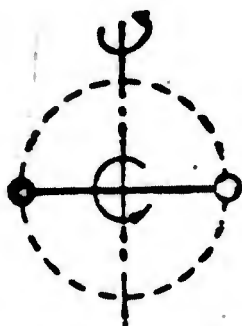
The monatomic molecule has the simplest structure.

Fig.5.20 - Rotational Motion of Diatomic Molecules

In studying the properties of a gas and in determining its energy level, the intraatomic motions (for example, the motion of the electrons) are usually not taken into consideration, and the atom is regarded as a material point. The motion of a monatomic molecule (or more precisely, its position in space) is therefore determined by three coordinates. We recall that the number of independent coordinates determining the position of a system in space is called the number of degrees of freedom of the system.

Thus a monatomic molecule has three degrees of freedom. These three degrees of freedom correspond to the displacement of the molecule in three mutually perpendicular directions, i.e., to its translational motion.

The more complex diatomic molecule (Fig.5.20) possesses a greater number of degrees of freedom. In fact, the state of a molecule consisting of two linked atoms is already determined by six coordinates, namely by the three coordinates determining the position of the center of gravity of the molecule in space, the two angles determining the position of the axis of the molecule in space, and, finally, by the coordinate characterizing the deviation of the atoms from their mean position in the molecule.

It is customary to correlate some form of motion with each degree of freedom of the molecule. Thus, the three degrees of freedom that correspond to the coordinates of the position of the center of gravity, are correlated with the translational motion of the molecules. The two degrees of freedom defining the position of the axis of the molecule in space are correlated with the rotation of the molecule about two axes not coinciding with the axis of the molecule. Here it would be meaningless to speak of the rotation of a molecule about its own axis, since we are considering the atoms as material points of infinitely small size. The coordinate defining the variation of interatomic distance is correlated with the oscillatory motion of the atoms in the molecule.

A triatomic molecule has a still a greater number of degrees of freedom, namely nine.

The internal energy of a gas U represents the sum of the energies of motion of the molecules with respect to each of its degrees of freedom. The magnitude of the internal energy thus depends on the number of degrees of freedom and on the intensity of molecular motion "with respect to the given degree of freedom".

It has been established that the only quantity determining the energy of motion of the molecules with respect to their degrees of freedom is the temperature. Consequently, the energy of motion with respect to a given degree of freedom U_i may be represented in the form of a certain function

$$U_i = \varphi(T).$$

(5.12)

The derivative

$$\frac{\partial U_i}{\partial T} = c_i$$

(5.13)

represents the rate of increase in energy for a given degree of freedom, with increasing temperature. If this derivative is related to 1° of temperature and to unit mass, for example to a gram-mole, then the quantity c_i will represent the heat capacity of the given degree of freedom, and will have the dimensions kcal/gm-mole deg. In this case, any degree of freedom is characterized by the fact that the heat
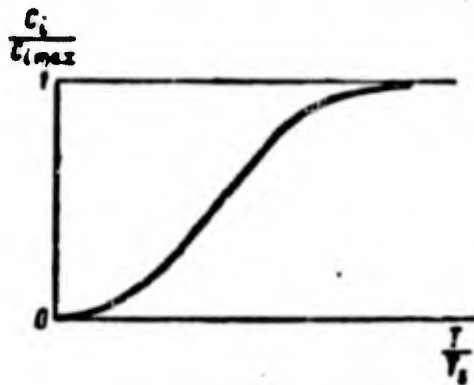

Fig.5.21 - Relation between the Ratio of the Heat Capacity for the ith Degree of Freedom, $\frac{c_i}{c_{i\ max}}$ and the Ratio of the Temperatures $\frac{T}{T_s}$

capacity c_i increases with temperature, but only up to a certain limit. At a certain temperature, the heat capacity for the given degree of freedom reaches its maximum value $c_{i\ max}$, after which it remains constant. This temperature may be termed the saturation temperature T_s. The character of the temperature dependence of the heat capacity for a given degree of freedom is shown in Fig.5.21.

The value of the maximum heat capacity $c_{i\ max}$, related to 1 gm-mole of gas, depends only on the form of the degree of freedom to which it is related and is completely independent of the individual properties of the gas. It has been theoretically shown and experimentally confirmed that the value of the maximum heat capacity for the translational and rotational degrees of freedom, related to 1 gm-mole of gas is $\frac{R}{2}$*, and that for the rotational degrees of freedom it is R, where R is the gas constant.

The degree of temperature at which saturation for the given degree of freedom is reached depends on the type of motion and on the properties of the given molecules.

* The value of R is here expressed in the same units as the heat capacity.

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72

The saturation for the translational degrees of freedom for all molecules without exception takes place at very low temperatures. Thus the heat capacity of the three translational degrees of freedom, i.e., the heat capacity of the translational motion of the molecule, is always constant, and is equal to $\frac{3}{2}$ R.

At a relatively high temperature (but also technically a very low one) at around 10 - 30° on the absolute scale, the saturation for the rotational degrees of freedom takes place, and their heat capacity likewise amounts to $\frac{R}{2}$ from this moment for each degree of freedom. As for the rotational degrees of freedom, their saturation for most of the diatomic and triatomic gases entering into the composition of the combustion product of rocket engines takes place only at very high temperatures, exceeding the combustion temperature. Thus the heat capacity for the oscillatory degrees of freedom is variable, and changes in such a way as to depend only on the temperature of the gas, increasing with that temperature.

The total heat capacity of any gas is composed of the heat capacities for all degrees of freedom possessed by a molecule of the given gas.

The heat capacity of monatomic gases, as will now be easily understood, remains constant over a wide range of temperatures and is equal to $\frac{3}{2}$R, while their internal energy is directly proportional to the temperature and is equal to $\frac{3}{2}$RT. The diatomic gases, at low temperatures (as related to the liquid-fuel rocket engine) possess the heat capacity of three translational and two rotational degrees of freedom, i.e., $\frac{5}{2}$ R, but at very high temperatures their heat capacity increases, approaching the value of $\frac{7}{2}$ R as a limit. Qualitatively, the same temperature dependence of the heat capacity of a gas also holds for triatomic gases.

We have considered above the so-called molar heat capacity of gases c, expressed in cal/gm-mole deg. The weight heat capacity

$$c_0 = \frac{c}{\mu} \text{ kcal/kg deg}$$

as demonstrated above, is of great importance in evaluating rocket engine fuels.

As pointed before, the heat capacity for each of the degrees of freedom and the energy for a given degree of freedom depend only on the temperature. For this reason, the internal energy likewise depends only on the temperature and is completely determined by the temperature. Consequently, this energy is a function of the state of the gas. This assertion is outwardly contradicted by the fact that the sum of the heat capacities of the degrees of freedom of the gas $\sum c_i$ is called the heat capacity at constant volume c_v, while the internal energy or, more precisely, its variation, is usually written in the form

$$U = \int_0^T c_v \, dT. \qquad (5.14)$$

Thus at first glance it might seem that the internal energy of a gas depends on the conditions (for example at constant volume or constant pressure) under which heat is transferred to the gas. In fact, however, the term heat capacity at constant volume has the meaning that, on heating a gas under the conditions $V = $ const, heat is consumed only to increase the internal energy of the gas and is not consumed for any other purpose.

The Heat Content of a Gas. The Adiabatic Index

The second function that characterizes the energetic state of a gas is the so-called heat content or enthalpy H.

The heat content is distinguished from the internal energy by the fact that the product pv or, expressed in heat units, Apv is added to the value of the internal energy. This product is a measure of the potential energy possessed by one kilogram of gas occupying the volume v at a pressure p. The heat content is therefore a criterion for the sum of the internal energy and the potential energy of the gas. For instance, the total energy of a compressed spring consists of the internal energy of the material of the spring, heated to the given temperature, and of the energy expended on its compression. This total energy of a compressed spring is analogous

to the heat content of a compressed gas. The name of this function obviously does not correspond to its physical meaning, since the quantity of heat possessed by a gas is determined by its internal energy.

The heat content is the most important energetic characteristic of a gas. This is due to the fact that, on a change of state of the gas in various technical processes, not only the internal energy but also the potential energy change in the vast majority of cases. Thus the total change in energy of a gas, taking place in various gas processes, is always determined by the magnitude of the change ΔH in the heat content.

By definition, the heat content is

$$H = U + Apv, \tag{5.15}$$

or, according to eqs.(5.7) and (5.14).

$$H = \int_0^T c_v \, dT + ART. \tag{5.16}$$

It is easy to see that the change ΔH in the heat content of a gas will correspond to the consumption of heat on heating the gas at constant pressure. With a rise in temperature from T_1 to T_2 and an expansion of the gas from the specific volume v_1 to v_2, the change in the heat content will be

$$\Delta H = \Delta U + p(v_2 - v_1)A.$$

Here $p(v_2 - v_1)$ represents the work of expansion of the gas under the pressure p. The derivative of the heat content with respect to temperature

$$\frac{dH}{dT} = c_v + AR = c_p \tag{5.17}$$

is termed the specific heat at constant pressure.

The value of the heat content, just like the value of the internal energy, is a function of the parameters of state of the gas. The change in heat content during any process does not depend on the form of the process and is determined only by the

initial and final states of the gas.

The heat content of liquid and solid substances (for example, of fuel components) is almost exactly equal to their internal energy, since, owing to the smallness of the specific volumes, the potential energy of compression is negligibly small.

We note that the specific heat c_p for all gases and at all temperatures is greater by the quantity AR than the specific heat c_v. In thermodynamics, the ratio of the specific heat at constant pressure to the specific heat at constant volume is of great importance. This quantity is called the adiabatic index and is denoted by k:

$$k = \frac{c_p}{c_v} = 1 + \frac{AR}{c_v}.$$

(5.18)

It follows from eq.(5.18) that the value of k depends on the specific heat of a gas at constant volume, i.e., on the structure and temperature of the gas. For the technical gases entering into the composition of combustion products, the value of k varies over a wide range as a function of temperature. With increasing temperature, the value of k decreases. For example, for diatomic gases, the value of k varies from 1.4 at low temperatures to 1.28 at very high temperatures.

The maximum values of k = 1.67 is possessed by monatomic gases, and the minimum value k = 1.15 by triatomic gases at high temperatures.

The specific heat at constant pressure may be expressed in terms of the adiabatic index k in the following manner:

$$c_p = \frac{k}{k-1} AR.$$

(5.19)

The internal energy, the heat content of a gas, or the respective heat capacities c_p and c_v, are calculated on the basis of experimentally determined molecular constants, using the methods of statistical thermodynamics. Over narrow temperature ranges, the variation in the heat capacity with temperature may be represented by

linear or power laws. Such relations, however, cannot be used over the entire range of temperature variation of the combustion products of liquid-fuel rocket engines.

Chemical Energy and Total Enthalpy

The Fundamental Equation of Combustion

During the combustion process, chemical energy is converted into thermal energy. For this reason, the value of the chemical energy must enter into the energetic characteristic of a fuel and of its combustion products.

The sum of the heat content and the chemical energy is termed the total enthalpy (or energy content). For a liquid, this will be the sum of the thermal chemical energies, and for gases it will be the sum of the thermal, potential, and chemical energies.

As noted above, the value of the chemical energy is not dependent on the external conditions but is determined only by the structure of the chemical substances participating in the reactions. The numerical value of the chemical energy depends on the system of reference adopted and, in particular, on the substances for which the chemical energy is considered to be zero.

If we assume, as is ordinarily done, that in the standard state (see above), the molecular gases and carbon in the form of β-graphite have a chemical energy equal to zero, then, for example for carbon dioxide gas we get a chemical energy of -94.05 kcal/gm-mole or -2410 kcal/kg. Water vapor likewise has a negative chemical energy equal to -57.80 kcal/gm-mole, or -3210 kcal/kg. The formation of these gases leads to the conversion of chemical energy into thermal energy.

Certain gases entering into the composition of combustion products, such as for example the atomic gases, have a positive chemical energy. This means that, on their formation, chemical energy is absorbed rather than liberated.

Making use of the concept of total enthalpy, it is easy to write the fundamental equation of combustion. For this we must apply the law of the conservation of

energy to the combustion process. Let us first assume that the combustion is not accompanied by any energy losses. Then the total heat content $I_{h.c}$ at a temperature T possessed by the gases as a result of the combustion process, must be equal to the total heat content I_T of the fuel entering the chamber;

$$I_{h.c} = I_T \tag{5.20}$$

Many energy losses may take place during the process of combustion, for example, those due to withdrawal of heat by the walls of the chamber, or those due the physical incompleteness of combustion with poor mixture formation. These may be taken into account by introducing the coefficient of complete combustion η_{cc}. The equation of combustion in this case may be written in the following form:

$$I_{h.c} = \eta_c I_T \tag{5.21}$$

To determine the temperature of combustion on the basis of eqs.(5.20) or (5.21), we must know the composition of the combustion products, since not only the chemical energy but also the heat content depends on the composition of the gas mixture (since the heat capacities of different gases are different).

The processes of dissociation exert a substantial influence on the composition of the combustion products and on the completeness of the conversion of chemical energy in the combustion chambers of liquid-fuel rocket engines.

4. Thermal Dissociation, and Composition of the Combustion Products

### Thermal Dissociation and the Equilibrium Constants

To describe the processes taking place in combustion chambers of rocket engines, and, in particular, of liquid-fuel rocket engines, we have paid particular attention to the questions of ensuring complete combustion of the fuel and, consequently, complete conversion of its chemical energy into thermal energy. The degree of completeness of the conversion of chemical energy into thermal energy, however, is determined not only by the design of the chamber and head, but also by

the specific features of the physical and chemical processes at high temperatures.

For combustion processes taking place at high temperatures, very intense thermal dissociation is characteristic: the processes of formation of chemical compounds on combustion under these conditions is partially accompanied by their dissociation.

When the reactions proceed in the opposite direction, an inverse transformation of energy takes place. As a result of dissociation, thermal energy losses occur, and the degree of utilization of chemical energy is decreased. For instance, at a high temperature, the oxidation reaction of carbon monoxide is necessarily accompanied by the inverse reaction of decomposition of carbon dioxide gas
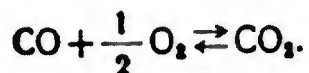
$$CO + \frac{1}{2} O_2 \rightleftarrows CO_2.$$

From the kinetic point of view, the possibility of an inverse reaction taking place is explained by the fact that, in the gas mixture, inverse collisions of the CO_2 molecules with each other or with molecules of CO and O_2, always take place which, at a sufficient force of impact, is accompanied by the decomposition of the CO_2 molecule into its components. In this case, the source of energy necessary to split the CO_2 is the energy of thermal motion.

As the combustion reaction proceeds, the number of original molecules, i.e., of CO and O_2, gradually decreases, so that the rate of this reaction also decreases. The rate of the dissociation reaction, on the other hand, increases with the content of combustion products in the gas (in our case CO_2), since the number of collisions in which CO_2 molecules participate will increase. As a result, a moment (and a state of chemical equilibrium) will arrive at which the rates of reaction of combustion and dissociation become equal. The mean chemical composition of the gas in this case will not vary.

The quantitative relationship established between the dissociated and undissociated gases under the conditions of chemical equilibrium are determined by the so-called chemical equilibrium constant, or equilibrium constant.

In liquid-fuel rocket engines, the equilibrium constants K_p used for the calculations are expressed in terms of partial pressures. Each partial pressure enters in the expression for the constant in the degree to which it influences the rate of the reaction. For example, the equilibrium constant of the reaction

$$CO_2 \rightleftarrows CO + \frac{1}{2} O_2$$
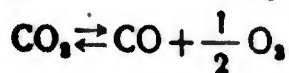
is expressed as follows:

$$K_p = \frac{p_{CO}\, p_{O_2}^{\frac{1}{2}}}{p_{CO_2}}, \qquad (5.22)$$

where p_{CO}, p_{O_2}, and p_{CO_2} are the partial pressures of the gases composing the given mixture, i.e., the pressures that these components would have if they occupied the entire volume of the mixture.

It will be clear from the expression presented for the equilibrium constant that the stronger the dissociation, the greater will be the value of K_p (the higher will be the pressures p_{CO} and p_{O_2}).

The value of the equilibrium constant K_p for a given reaction depends only on the temperature. This relation is exceedingly complex, and for the reactions between combustion products of rocket engines, it is impossible to present analytic expressions relating the equilibrium constants and the temperature.

The equilibrium constant today is calculated by the methods of statistical thermodynamics. In order to calculate the equilibrium constant, it is necessary to know the molecular constant and, chiefly, the values of the chemical energies of the corresponding substance. Tables giving values of the equilibrium constants, compiled for the necessary range of temperature variation, are used in such calculations.

Influence of Temperature and Pressure on the Composition of Combustion Products

The values of the equilibrium constants of the dissociation reactions increase

sharply with increasing temperature, and the content of the dissociation products in the combustion products increases accordingly. This is also obvious from the kinetic point of view. If the temperature T of the gas mixture is increased, then the number of molecules with a large energy reserve will also increase, which will lead to an increase in the rate of dissociation of the combustion products and to a disturbance of the equilibrium established at the former temperature. At the new and higher temperature of the gas, the equilibrium state is again established and is characterized by the equality of the rates of forward reaction (combustion) and inverse reaction (dissociation) but, this time, with a higher content of dissociation products in the gas mixture. Thus the temperature of the gas mixture will have an effect on the composition of this mixture, such that, with increasing temperature, the content (in the mixture) of gases whose formation requires the consumption of heat will increase with increasing temperature.

The equilibrium constant for ideal gases does not depend on the pressure; however, this does not mean that the composition of a gas mixture will always remain constant at variations in pressure.

Many dissociation reactions are accompanied by a change in the volume of the gas mixture. For example, on dissociation of carbon dioxide gas, the number of moles will increase, but this means that the volume of the gas mixture will also increase by 1/2 mole for each mole of completely dissociated carbon dioxide gas.

For dissociation reactions taking place with an increase in the number of moles, the composition of the gas mixture will depend on the pressure. In this case, an increase in pressure will lead to suppression of the dissociation reactions and to an increase in the content of complete combustion products in the gas mixture. In other words, an increase in pressure will decrease the degree of dissociation of gases if it is accompanied by an increase in the number of moles. For dissociation reactions that proceed without a change in the number of moles, the composition of the products does not depend on the pressure. Since most reactions of dissociation

of the combustion products of rocket fuels involve an increase in the number of moles, it follows that an increase in the combustion pressure will somewhat decrease the degree of dissociation (not very substantially).

Composition and Temperature of the Combustion Product in Rocket Engines

Completeness of Liberation of Chemical Energy

The usual rocket-engine fuels consist of four elements: carbon, hydrogen, oxygen, and nitrogen.

If combustion were not accompanied by dissociation, then the combustion prod-
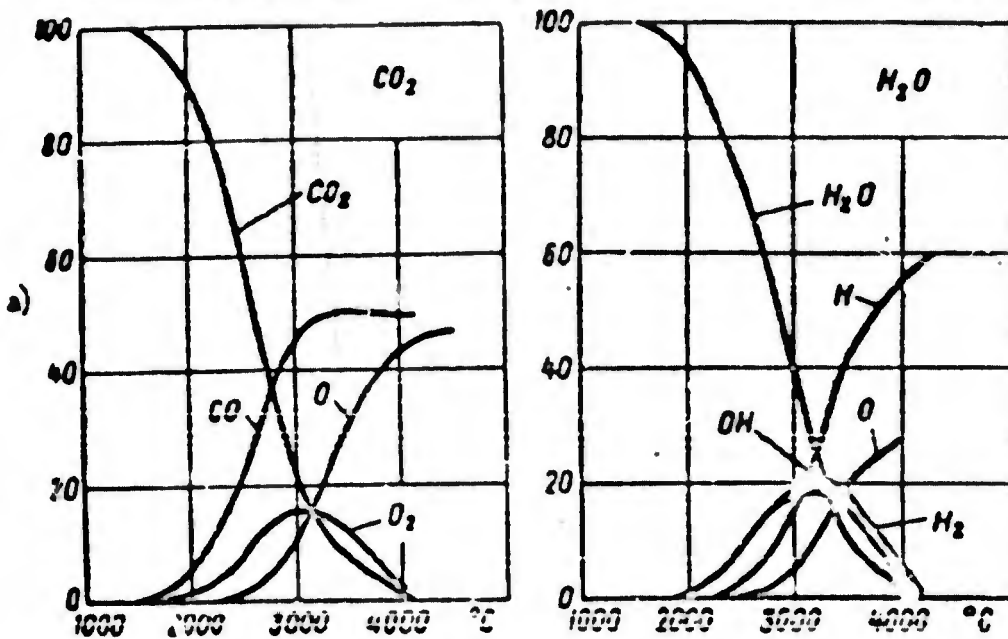
Fig.5.22 - Dissociation of Water Vapor H_2O and Carbon Dioxide

Gas CO_2 as a Function of Temperature

a) Percent by volume

ucts would consist of carbon dioxide gas CO_2, water vapor H_2O, and molecular nitrogen N_2*. However, even at "moderate" temperatures (about $2800°$ abs), a considerable dissociation of carbon dioxide and water vapor is already noted (Fig.5.22).

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* At a stoichiometric ratio of the components.

In this case, carbon monoxide CO, the hydroxyl group OH, and molecular oxygen and hydrogen O_2 and H_2 are also formed. At a still higher temperature, the content of nitrogen oxide NO, and of the atomic gases hydrogen H, oxygen O, and nitrogen N in the combustion products, becomes substantial.

The composition of the combustion products in the chamber is determined by the equilibrium constants of the corresponding dissociation reactions, taking account of the pressure p_k in the chamber. The composition of the gases, of course, also depends on the relative content of the various elements in the fuel.

Since the composition of the combustion products is temperature-dependent, the solution of eqs.(5.20) or (5.21) requires a rather great amount of computing work. Ordinarily, the value of the temperature must be established and the equilibrium
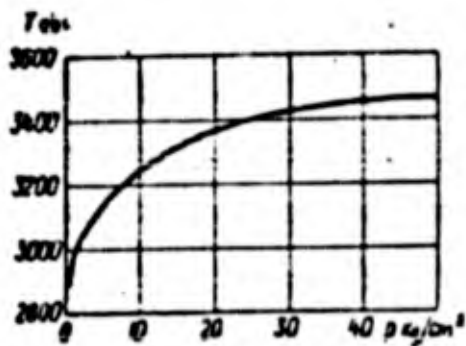

Fig.5.23 - Pressure Dependence of the Temperature of the Combustion Products of an Oxygen + Kerosene Fuel at α = 0.7
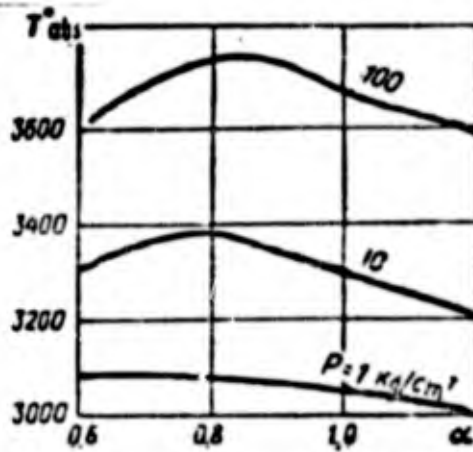
Fig.5.24 - Dependence of Combustion Temperature of an Oxygen + Kerosene Fuel on the Coefficient of Excess Oxidizer α and on the Pressure p

constants and fuel composition must then be used in determining the composition of the combustion products, i.e., the partial pressures of the gases; finally, the fundamental equation of combustion must be verified:

$$I_{n.o} = \eta_{oc} I_{\tau}.$$

The true temperature and the corresponding composition of the combustion products are thus determined by the method of selection.

The calculation results show that, because of the sharp increase in the degree of dissociation of the combustion products with increasing temperature above 3000° abs, an increase in the supply of chemical energy in the fuel does not lead to a proportional increase in the temperature of the chamber. For example, the combustion temperatures of two fuels can be compared: kerosene + nitric acid, and kerosene + oxygen. The calorific value of the latter fuel amounts to 2400 kcal/kg, which is about 70% greater than the calorific value of the former fuel (1400 kcal/kg). But the temperature of combustion of the kerosene + oxygen fuel (3550° abs) is only 15% higher than the combustion temperature of kerosene with nitric acid (3050° abs). This is a direct consequence of the intense dissociation of the combustion product and of the decreased completeness of liberation of chemical energy.

Consider further the dependence of the combustion temperature on the pressure.

This dependence is well illustrated by the graph in Fig.5.23, constructed for the combustion product of the fuel kerosene + liquid oxygen at $\alpha = 0.7$. It will be seen from this relation that at first, at low absolute values, an increase in pressure leads to a rapid rise in temperature, but then, with increasing pressure, to an ever slower rise in temperature.

Not only the pressure, but also the ratio of the fuel components affects the temperature and composition of the combustion products.

Without taking account of the dissociation, the combustion temperature and the quantity of heat liberated on combustion would reach their maximum values at the theoretical ratio of the fuel and oxidizer v_0, i.e., at $\alpha = 1$. But the phenomenon of dissociation decreases the combustion temperature, while the nonuniform stability of the combustion products with respect to dissociation causes the maximum temperature and maximum heat liberation to correspond to values of $\alpha < 1$ for modern liquid-fuel rocket engine fuels, i.e., to propellants with a deficiency of oxidizer

and an excess of combustible.

Figures 5.24 and 5.25 show the dependence of the combustion temperature and the quantity of heat liberated Q for an oxygen + kerosene propellant on the coefficient of oxidizer excess α and on the pressure. The shift in the temperature maxima and in the heat-liberation maxima toward α < 1 is explained by the fact that, with a deficiency of oxidizer, the relative content of carbon monoxide, stable to dissociation, in the combustion products will increase. As shown by the curves in
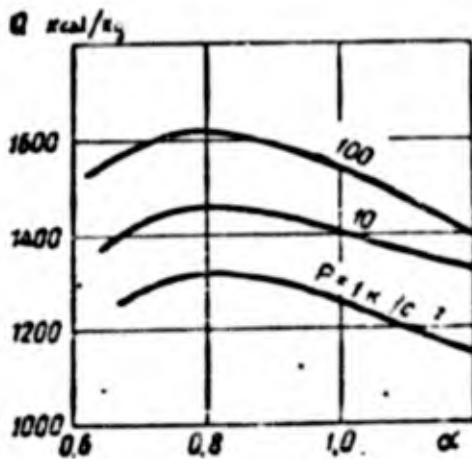

Fig.5.25 – Dependence of the Heat Liberation on Combustion of an Oxygen + + Kerosene Propellant on the Coefficient of Excess Oxidizer α and on the Pressure p
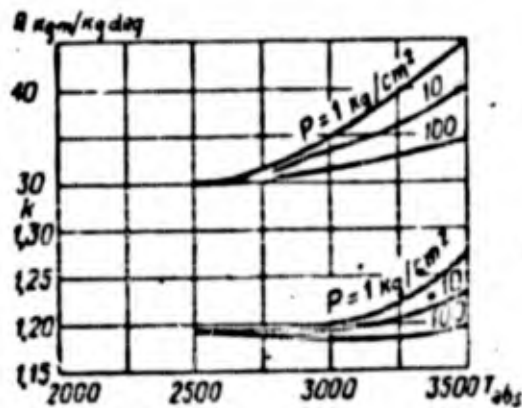
Fig.5.26 – Dependence of the Gas Constant of the Combustion Products R, and of the Adiabatic Index k, on the Temperature T and the Pressure p

Fig.5.25, the heat losses due to dissociation in the combustion chamber are rather high, amounting to over 30% of the calorific value of the fuel, or 2400 kcal/kg, at a pressure of 10 kg/cm² in the chamber.

We have been discussing the influence of dissociation from the example of a fuel with the maximum value of calorific power. Since the intensity of dissociation decreases with decreasing temperature, the influence of dissociation decreases for fuels with a lower heat value (oxygen + alcohol, or nitric acid + kerosene), although it still remains rather substantial. For example, the heat loss in the

chamber, due to dissociation, for an oxygen + alcohol propellant amounts to 18 - 25% of the heat value, and for fuels containing nitrogen and oxygen, to 12 - 18%.

The composition of the combustion products determines the value of their gas constant. The combined influence of composition and temperature on the specific heat of gases leads to a corresponding change in the exponent of adiabatic of curve k. The influence of the temperature and pressure of the combustion products on the value of the gas constant R, and on that of the exponent of adiabatic curve k, is illustrated by the graph in Fig. ⸱. 26. As shown by this graph, the gas constant of the combustion product increases with increasing temperature. This is a consequence of the decreased content of polyatomic gases in the combustion products, which is a result of dissociation. For this same reason, the adiabatic curve of the combustion products increases with increasing temperature and decreasing pressure.