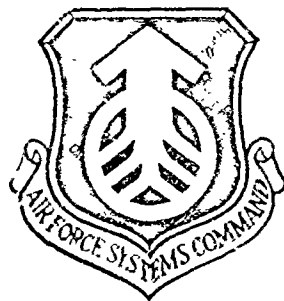


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BURNING OF HETEROGENEOUS CONDENSED SYSTEMS

by

N. N. Bakhman and A. F. Belyayev

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By: N. N. Bakhman and A. F. Belyayev

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ABSTRACT Heterogeneous condensed systems constitute mechanical mixtures of solid or viscous liquid fuels and oxidizers.

Among systems of this type, the most interesting at present are mixed solid fuels (for rocket, jet and other engines) and pyrotechnic mixtures (for greater detail see [159, 222, 223 and others]).

Neither of these classes of condensed mixtures is new. Actually, the history of application of black powder as a rocket fuel, and also application of different pyrotechnic mixtures dates back many centuries. However, toward the end of the nineteenth century, black powder lost its value as a rocket fuel, at first in connection with temporary fall of interest toward rocket technology, and then, after the beginning of the fast development of rocket technology in the twenties of our century, in connection with the appearance of liquid-propellant rocket engines and engines on solid fuel of the ballistite type. Regarding pyrotechnic mixtures, interest toward them was constantly preserved, but in connection with the comparatively limited volume of their production, investigation of regularities of burning of pyrotechnic mixtures was conducted on small scales. Furthermore, it was strongly hampered by the very large variety of properties of components of different pyrotechnic mixtures.

It is natural, therefore, that the theory of burning (development of which started in the nineties of last century) was developed first of all in reference to the burning of gases, which has great practical value and is considerably simpler in its regularities. It is also necessary to consider that during investigation of the burning of gases, there can be used many results obtained during the study of the kinetics of gas reactions in the region of lower temperatures.

Later it was established that the thermal theory of burning of gases can be successfully used to describe the burning of volatile homogeneous

condensed systems. For nonvolatile homogeneous systems, the conclusions of the thermal theory of burning were used mainly in reference to reaction in the condensed phase. These conclusions were supplemented with a number of qualitative presentations (first of all about the presence of dispersion on the surface of a burning charge).

Interest toward heterogeneous condensed systems and the volume of corresponding investigations was considerably increased in the fifties in connection with the fast development of mixed solid rocket propellants of different types.

At present in literature, there are at least several tens of works concerning burning of heterogeneous systems. Using the results of these works and leaning on the conclusions of the thermal theory of burning, it is possible to construct qualitative presentations about the burning of heterogeneous condensed systems and the elements of quantitative theory. English Translation: 214 pages.

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INTRODUCTION

Heterogeneous condensed systems constitute mechanical mixtures of solid or viscous liquid fuels and oxidizers.

Among systems of this type, the most interesting at present are mixed solid fuels (for rocket, jet and other engines) and pyrotechnic mixtures (for greater detail see [159, 222, 223 and others]).

Neither of these classes of condensed mixtures is new. Actually, the history of application of black powder as a rocket fuel, and also application of different pyrotechnic mixtures dates back many centuries. However, toward the end of the nineteenth century, black powder lost its value as a rocket fuel, at first in connection with temporary fall of interest toward rocket technology, and then, after the beginning of the fast development of rocket technology in the twenties of our century, in connection with the appearance of liquid-propellant rocket engines and engines on solid fuel of the ballistite type. Regarding pyrotechnic mixtures, interest toward them was constantly preserved, but in connection with the comparatively limited volume of their production, investigation of regularities of burning of pyrotechnic mixtures was conducted on small scales. Furthermore, it was strongly hampered by the very large variety of properties of components of different pyrotechnic mixtures.

It is natural, therefore, that the theory of burning (development of which started in the nineties of last century) was developed first of all in reference to the burning of gases, which has great practical value and is considerably simpler in its regularities. It is also necessary to consider that during investigation of the burning of gases, there can be used many results obtained during the study of the kinetics of gas reactions in the region of lower temperatures.

Later it was established that the thermal theory of burning of gases can be successfully used to describe the burning of volatile homogeneous condensed systems. For nonvolatile homogeneous systems, the conclusions of the thermal theory of burning were used mainly in reference to reaction in the condensed phase. These conclusions were supplemented with a number of qualitative presentations (first of all about the presence of dispersion on the surface of a burning charge).

Interest toward heterogeneous condensed systems and the volume of corresponding investigations was considerably increased in the fifties in connection with the fast development of mixed solid rocket propellants of different types.

At present in literature, there are at least several tens of works concerning burning of heterogeneous systems. Using the results of these works and leaning on the conclusions of the thermal theory of burning, it is possible to construct qualitative presentations about the burning of heterogeneous condensed systems and the elements of quantitative theory.

CHAPTER I

BASIC PROCESSES DETERMINING RATES OF COMBUSTION FOR VARIOUS TYPES OF FLAMES

In general, burning rate depends on speed of mixing of initial components in the zone of heating and in the zone of reaction (for heterogeneous systems), on speed of chemical reactions between components, on speed of transmission of heat and active particles from zone of reaction to initial system. Normal burning rate (and all the more so form of front of burning) depends on conditions of flow of fresh mixture* and products of burning (especially during burning in engines).

Naturally, there cannot be speech about creation of a formula useful for all cases which allows calculating burning rate or even speech about recording of a single system of equations useful for numerical solution for all cases, which, at the same time, is not too awkward.

Therefore, in the theory of burning, there are examined several basic types of flames. They are unequal in their scientific and practical value and degree of mastery. The parameters which are the most interesting for a given type of flame are unequal. The approach to theoretical consideration of every type of flame essentially differs. There are certain distinctions in experimental methods.

Let us enumerate the most important types of flames for the theory of burning: 1) laminar flame in homogeneous gas mixture. To this type there belongs the flame during burning of volatile explosives;

2) laminar diffusion flame during the burning of a stream of combustible gas in an oxidizing atmosphere. To this type there adjoins the flame during diffusion burning of liquid fuel poured into a cylindrical vessel, etc.;

3) the flame during burning of a drop of liquid fuel or particle of solid fuel in an oxidizing atmosphere;

*For gaseous systems or systems of gas and solid particles (or liquid drops).

4) turbulent flames in homogeneous or in gas mixtures not mixed preliminarily;

5) flame during burning of nonvolatile explosives, powders, etc., in those cases, when an essential role is played by the reaction in the condensed phase.

There is a great number of intermediate cases, for example, burning of a suspension of particles of solid fuel or of a suspension of drops of liquid fuel or of a suspension of drops of liquid fuel in the flow of a gaseous oxidizer (this case combines in itself criteria characteristic for flames of type 3 and 1 or 3 and 4). The greatest technical interest is presented by, namely, the intermediate cases.

Burning of condensed mixtures also constitutes an intermediate case, in which there can, in this or that degree, be combined criteria characteristic for flames of type 1, 2, 3 and 5. Turbulence can also play a definite role during the burning of condensed mixtures, however, in completely different conditions as compared to the flames of type 4.

We will briefly examine certain characteristics of the basic types of flames to the extent that this is useful in understanding the regularities of burning of condensed mixtures.

Preliminarily one should stop on determination of burning rate. During laminar burning of gas mixtures and homogeneous condensed systems, the idea of normal burning rate (u_H) has great fundamental value. By definition u_H is equal to speed of shift of flame relative to fresh mixture in a direction perpendicular to the surface of the flame at a given point. Dimension u_H is in [SI] (CM) — m/s; however, for the burning rate, this unit is rarely used up to now and is used only for gas systems. Usually value u for gas systems is expressed in cm/s, and for condensed systems in mm/s (if one were to express burning rate of condensed systems in m/s, then in the usual range of pressures, there would be obtained very small fractions).

For homogeneous condensed systems, there is most frequently measured the burning rate of cylindrical charges burning from the end where the front of burning is assumed planar (experience will show that in most cases in the presence of the proper shell, this assumption is valid, and distortions are observed only at the edges of the charge). Moreover, for solids (and sufficiently viscous liquid substances), the initial (solid or liquid) substance is stationary during burning. Therefore, in this case, the normal burning rate is simply equal to the apparent velocity of the flame (in a laboratory system of coordinates) and is constant at different points of the charge.

Things are approximately the same during measurement of the burning rate of a gas mixture on a flat burner, the only difference being that in this case the front of burning is stationary and the fresh mixture moves with speed $u = v_H = V/S$, where V is volumetric flow rate of gas through the burner, cm^3/s ; S is the cross section area of the burner, cm^2 . The analogy is all the more complete when volatile [VV] (BB) at first evaporate, and flow of vapors burns in front of burning (however, for condensed substances, burning rate is measured relative to the condensed phase, and not relative to the gas phase).

During measurement of the burning rate of a gas mixture with the help of a Bunsen burner, the front of burning has a coneshaped form (Fig. 1),

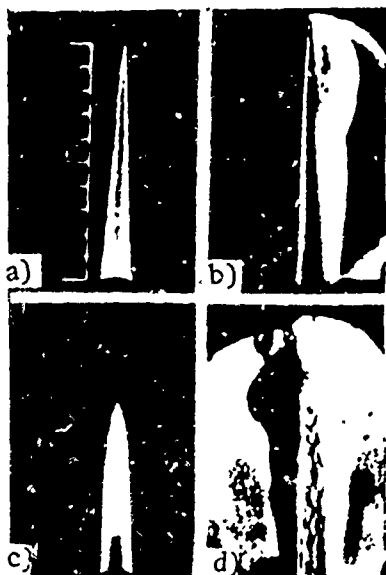


Fig. 1. Laminar (a, b) and turbulent (c, d) flame in a stoichiometrical mixture of natural gas with air [50]: a, c — usual photograph with prolonged exposure; b, d — schlieren photograph with a very short exposure.

and the area of its surface S_ϕ is considerably larger than the area of cross section of the burner. Normal burning rate (average) is equal to $u_H = V/S_\phi$. It is also possible to express u_H through speed, v , of gas flowing to the front of burning: $u_H = v \sin \phi$, where ϕ is the angle between the velocity vector of the gas and the front of burning.

During burning of a gas mixture in pipes or spherical vessels, apparent velocity of the flame (with respect to the walls of the vessel) is not equal to normal burning rate, since under the influence of expansion of the products of combustion, fresh mixture before the front of burning moves with respect to the vessel walls.

Thus, measurement of normal burning rate u_H is simplest for homogeneous condensed systems, since in this case the front of burning is planar and the parent substance is stationary (in a laboratory system of coordinates); therefore, u_H is equal to apparent velocity of flame propagation u (in a laboratory system of coordinates).

It is necessary, however, to emphasize that the idea of normal burning rate can be used for all types of flames (see below). In particular, for the case of condensed mixtures which interests us most, the surface of the front of burning has a complex nonstationary form, and it is impossible to measure its value. Therefore, for condensed mixtures under burning rate there is implied apparent velocity of shift of the whole zone of burning (in a laboratory system of coordinates), no matter what the thickness of this

zone and the surface of front of burning. Only in the maximum case of sufficiently finely divided mixtures of volatile components, when burning takes place analogously to burning of homogeneous systems, is the burning rate the normal burning rate. Besides the linear burning rate, there is also used the mass burning rate $m = \rho u$, where ρ is density of fresh mixture. It is obvious that m is equal to the mass of substance burning in a unit of time on a unit of area of the front of burning (if u_H is taken) or on a unit of area of cross section of charge (if u is taken). In the International unit system, the dimension of mass speed is $\text{kg/m}^2 \cdot \text{s}$; however, in literature this unit has not been encountered,* up to now, and value m is expressed in $\text{g/cm}^2 \cdot \text{s}$ ($1 \text{ g/cm}^2 \cdot \text{s} = 10 \text{ kg/m}^2 \cdot \text{s}$).

As for gas, so also for condensed systems, mass burning rate is used more rarely than linear burning rate. This is partly combined with the fact that experimentally, as a rule, the linear burning rate is measured.

However, during comparison of burning rate of gas and condensed systems, only mass burning rate is appropriate. Really, value m for gas mixtures and volatile condensed substances has the same order. Conversely, burning rate at low pressures for gas mixtures is several orders higher than for condensed systems (in order to process an identical quantity of substance in the zone of reaction in a unit of time, it is necessary to pass a gas with greater speed than the density of the gas).

Furthermore, it is necessary to consider that for condensed systems, the mass burning rate depends on pressure p according to the same law on which the linear burning rate depends, and differs from her only by a constant fact (since the density of condensed systems in the interval of pressure which interest us practically does not depend on p). Accordingly, if one were to approximate function $u(p)$ with the help of exponential function $u = bp^v$, then exponent v would be the same for the linear and the mass burning rate.

Conversely, for gas systems, the density of which is proportional to pressure, exponent v for the mass burning rate will be larger per unit than for the linear burning rate. Therefore, in order to compare data for gas and condensed systems, we will use mass burning rate** for gas systems.

*Let us note that if burning rate is taken in mm/s and density is taken in g/cm^3 , then for the mass burning rate we will obtain a value corresponding to units of the international unit system: $1 \text{ mm/s} \cdot \text{g/cm}^3 = 10^{-3} \text{ m/s} \cdot 10^{-3} \text{ kg/10}^{-6} \text{ m}^3 = 1 \text{ kg/m}^2 \cdot \text{s}$.

**Usually the composition of gas mixtures is given in volume percentages. Accordingly, the density of gas mixtures can be conveniently calculated by the formula:

$$\rho_{\text{мисш}} = (p/RT) \cdot \sum_i \theta_i \mu_i,$$

where $\theta_i = V_i / \sum_i V_i$ is the volume part of the i -th gas, and μ_i is the molecular weight of the i -th gas.

§ 1. Laminar Flame in Homogeneous Gas Mixtures

This type of flame has been studied in considerably greater detail and considerably deeper than any other type of flame.

The flame in a homogeneous mixture (laminar and turbulent) presents considerable practical interest in connection with questions of safety of works in coal mines, and also exploitation of all possible capacities and main lines filled with combustible gas and volatile liquid; in connection with investigation of work of certain types of gas burners, etc.

The laminar flame in homogeneous mixtures has especially great value for the theory of burning, since for this type of flame, the influence of chemical factors does not darken processes of mixing of initial components, and the field of speeds of fresh mixture can be very simple.

There have been investigated several different forms of laminar homogeneous flame. Burners of different constructions are most frequently used. Figure 1 shows a Bunsen burner flame, and Fig. 2 shows a flat porous burner flame.

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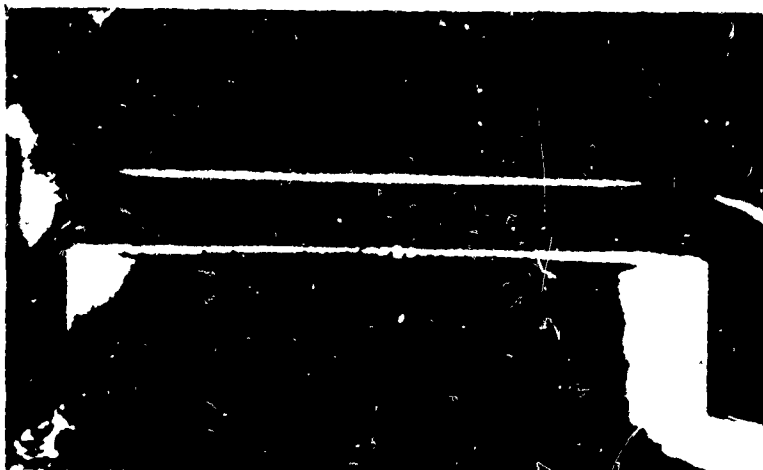


Fig. 2. Flat flame (ethylene - air) on a porous burner [20]. The field of speeds of the gas is traced with the help of small particles (~4 microns).

In these cases the flame is stationary in the laboratory system of coordinates, thanks to which it is convenient to measure not only burning rate, but also profiles of temperature and concentration (with the help of optical methods, thermocouples, sampling of gas, etc.).

There has also been investigated propagation of flame in pipes and spheric vessels with rigid walls ("bombs of constant volume") or elastic walls ("bombs of constant pressure"). In this case both front of burning and fresh mixture move in a laboratory system of coordinates; therefore, measurement of profiles of temperature and concentration are very hampered. However, these methods have essential advantages during measurement of speed of flame at high pressures.

Let us consider now the data available in literature on burning rate of gas mixtures. We will use only normal burning rate; however, for brevity of recording instead of u_H ; $(u_H)_{\max}$, $\alpha(u_H)_{\max}$, etc., we will write u , $u_{\max}$, $\alpha_{u_{\max}}$, etc.

We have taken part of the experimental data (from works [2, 3, 6] and others) from graphs. The values of index v in formula $m = bp^v$ and the value of temperature coefficient $\beta_m = d \ln m / dT_0$ have also been calculated by us from experimental data given in quoted works.

A. Absolute Velocity of Burning

Let us first give data on maximum burning rates and burning rates of stoichiometrical mixtures (for the overwhelming majority of gas mixtures, $(u_H)_{\max}$ and $m_{\max}$ is attained at a mixture ratio not too far from the stoichiometrical mixture ratio — see below).

The main part of experimental data pertains to air mixtures at atmospheric pressure. In this case, according to survey work data [1], for a majority of combustible gases studied (approximately 45 out of 60) value $m_{\max}$ lies

within limits $0.03-0.06 \text{ g/cm}^2 \cdot \text{s}$. Only for hydrogen and low-molecular unsaturated and cylindrical compounds does value $m_{\max}$ reach $0.1-0.2 \text{ g/cm}^2 \cdot \text{s}$. (Table 1).

Table 1. Maximum Mass Burning Rates, Mass Burning Rates of Stoichiometrical Mixtures and Combustion Temperature of Stoichiometrical Gas Mixtures at Atmospheric Pressure and Room Temperature

Combustible gas	$m_{\max}, \text{g/cm}^2 \cdot \text{s}$		$m_{\alpha=1}, \text{g/cm}^2 \cdot \text{s}$		Design temperature of burning, t_k	
	mixtures with air	mixtures with oxygen	mixtures with air	mixtures with oxygen	mixtures with air ($\alpha=1$)	mixtures with oxygen ($\alpha=1$)
Hydrogen. . .	0,198 [1]	0,385 [8]	0,148 [10]	—	2345 [10]	—
Acetylene	0,186 [1]	—	0,165 [4]	1,16 [9]	2370 [11]	3050 [11]
Ethylene oxide	0,113 [1]	—	0,173 [10]	—	2580 [10]	—
Ethylené . . .	0,088 [1]	—	0,112 [10]	—	2520 [11]	3320 [11]
Carbon monoxide	0,0616 [1]	—	0,072 [4]	0,761 [4]	2425 [10]	—
	0,051 [2]	0,125 [2]	0,089 [10]	0,645 [9]	2340 [10]	3170 [12]
	0,055 [8]	0,135 [8]	—	—	—	—
Benzene. . . .	0,06 [1]	0,46 [3]	0,037 [8]	0,135 [8]	2570 [8]	2970 [11]
Propane . . .	0,057 [1]	—	0,06 [10]	0,46 [3]	2340 [10]	—
	—	—	0,041 [4]	—	—	—
Methane. . . .	0,052 [1]	0,512 [2]	0,054 [10]	—	2260 [10]	—
	0,038 [2]	0,367 [8]	0,0377 [4]	0,415 [4]	2200 [10]	—
	0,0347 [5]	—	0,045 [10]	—	2220 [8]	—
	0,0435 [6]	—	—	—	—	—
	0,0425 [7]	—	—	—	—	—

It was possible to distinctly trace the influence of molecular structure of fuel on burning rate for low-molecular hydrocarbons with a direct chain [13]. In this case burning rate increases with increase of degree of nonsaturation of bonds in the molecule (burning rate increases in the series, alkanes < alkenes < alkadienes < alkynes) (Fig. 3). With increase of length of chain, this effect decreases (Fig. 4), but, all the same, the burning rate of air mixtures for n-hexine is approximately 25% higher than for n-hexane.

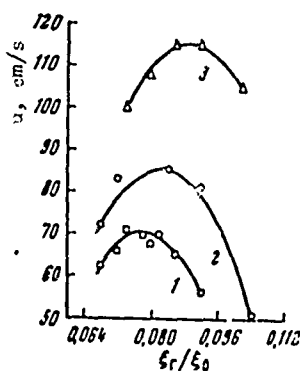


Fig. 3.

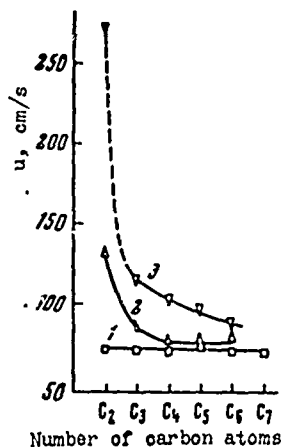


Fig. 4.

Fig. 3. Dependence of burning rate on the ratio between fuel and oxidizer for mixtures of propane (1), propylene (2) and propyne (3) with air at $p = 1$ [atm(abs.)] [13].

Fig. 4. Maximum burning rate in air mixtures of n-alkanes (1), n-alkenes (2), and n-alkynes (3) depending upon length of chain [13].

Data for oxygen mixtures (at 1 [atm(abs.)]) are much less abundant. The burning rate for oxygen mixtures is considerably higher than for air mixtures (2-3 times for hydrogen and carbon monoxide, but for methane — more than an order; see Table 1). The mass burning rate of oxygen mixtures studied lies within limits of $0.4-1.2 \text{ g/cm}^2 \cdot \text{s}$ (with the exception of $\text{CO} + \text{O}_2$ mixture, for which it is $m_{\text{max}} \approx 0.125 \text{ g/cm}^2 \cdot \text{s}$).

Data for a flame from oxides of nitrogen (Table 2) are also interesting.

From Table 2 it is clear that burning rate for mixtures on an NO base is essentially lower than for air mixtures (to say nothing of oxygen). For mixtures on an NO_2 base burning rate is close to the burning rate of air mixtures. Finally, burning rate of mixtures on a nitrous oxide base occupies an intermediate position between burning rates of oxygen and air mixtures, but still lies nearer to the latter.

Table 2. Mass Burning Rate of Homogeneous Gas Mixtures ($\alpha = 1$) on the Basis of Oxides of Nitrogen at Atmospheric Pressure and Room Temperature ($p = 1$ atm).

Fuel	Oxidizer				
	N ₂ O [9]	NO [9]	NO ₂ [9]	O ₂	Air
H ₂	0,382	0,02	0,103	0,575 [4]	0,148 [10]
C ₂ H ₂	0,273	0,106	0,226	1,16 [9]	0,173 [10]
C ₂ H ₄	0,208	0,073	0,079	0,645 [9]	0,089 [10]
C ₂ H ₆	0,155	0,029	0,035	0,394 [9]	0,053 [11]

For mixtures on the basis of hydrogen, data are [11, 12] according to combustion temperature (Table 3).

Table 3. Burning Rate and Combustion of Stoichiometrical Mixtures of Hydrogen with Different Oxidizers at Atmospheric Pressure

	Oxidizer			
	N ₂ O	NO	O ₂	Air
$m, \text{g/cm}^2 \cdot \text{s} \dots$	0,382 [9]	0,02 [9]	0,575 [4]	0,148 [10]
$T_r (\text{design}) ^\circ\text{K}$	2960 [11]	3110 [12]	3050 [11]	2345 [10] 2370 [11]

From Table 3 it is clear that the burning rate of an H₂ + NO mixture is at least an order lower than that speed which was to be observed for this mixture, if there existed a simple connection between combustion temperature and burning rate.

It is necessary to note that for flames on the basis of NO₂, there are usually observed two zones of burning [12]. In the first zone, NO₂ breaks up into NO + $\frac{1}{2}$ O₂, and oxygen reacts with fuel. In the second high-temperature zone, NO reacts with fuel. Two zones of reaction are observed in certain cases for NO — hydrocarbon flames. In this case in the first zone disintegration of NO (with subsequent reaction between oxygen and hydrocarbon) goes as a result of interaction with CH, CN, NH, etc, radicals. In the second zone, where temperature is already sufficiently high, thermal disintegration of NO becomes essential.

We will also give data for flames of disintegration of endothermic compounds (in gas phase at atmospheric pressure): ozone [14] ($T_0 = 27^\circ\text{C}$); hydrazine [15] ($T_0 = 150^\circ\text{C}$), ethylene oxide [16] ($T_0 = 25^\circ\text{C}$) and acetylene [18] (at 2 [atm(abs.)]).

$m, \text{ g/cm}^2 \cdot \text{s} \dots\dots 0,927$ O_2 N_2 C_2H_2 C_2H_4
 $T_r \text{ (design), } ^\circ\text{K. } 2677$ 1950 1217 2530^{**}

*In work [17] there was obtained $m = 0.0225 \text{ g/cm}^2 \cdot \text{s}$.

**Neglecting radiation losses by carbon particles.

At high pressures, data are not numerous (in comparative detail, there was studied only a methane-air mixture; Table 4). Let us note that at high pressures, the difference between burning rates of oxygen and air mixtures increases still more.

Table 4. Maximum Burning Rates of Gas Mixtures at High Pressures

Mixture	$m_{\text{max}}, \text{ g/cm}^2 \cdot \text{s}$					
	5 atm	10 atm	20 atm	40 atm	60 atm	90 atm
$\text{H}_2 - \text{O}_2$	4,5 [4] *	—	—	—	—	211 [2]
$\text{CH}_4 - \text{O}_2$ [2]	—	—	15,5	—	—	67,3
$\text{CO} - \text{O}_2$ [2]	0,70	—	4,18	—	10,6	15,3
$\text{H}_2 - \text{NO}$ [2]	0,23	—	1,29	—	—	—
$\text{C}_2\text{H}_2 - \text{air}$ [4] *	0,88	1,74	—	—	—	—
$\text{C}_2\text{H}_4 - \text{air}$ [4] *	0,32	0,69	1,02	—	—	—
$\text{CO} - \text{air}$ [2]	—	—	0,79	—	—	1,82
$\text{CH}_4 - \text{air}$	0,13 [4] *	0,29 [4] *	0,21 [2]	0,23 [5]	0,29 [5]	0,51 [2]
	0,11 [6]	0,14 [5]	0,29 [4] *	0,25 [7]	—	—
(decomposition)	0,11 [7]	—	0,21 [7]	—	—	—
$\text{C}_2\text{H}_2 - \text{position}$	0,09 [19]	0,094 [18]	—	—	—	—
$\text{C}_2\text{H}_4 - \text{(decomposition)}$	—	0,033	0,07	0,145	—	—

*Instead of $m_{\text{max}} m_\alpha = 1$ is given.

B. Burning Rate as a Function of the Fuel to Oxidizer Ratio

It is of interest to clarify at what mixture ratio burning rate is maximum and how fast it decreases with deviation from this composition. The fuel to oxidizer ratio can be conveniently characterized by the coefficient $\alpha = (\xi_{\text{OK}}/\xi_r)/(\xi_{\text{OK}}/\xi_r)_{\text{cr}} = (\vartheta_{\text{OK}}/\vartheta_r)/(\vartheta_{\text{OK}}/\vartheta_r)_{\text{cr}}$, where ξ_{OK}, ξ_r are parts by weight, and $\vartheta_{\text{OK}}, \vartheta_r$ are parts by volume of oxidizer and fuel in a given mixture; $(\xi_{\text{OK}})_{\text{cr}}, (\xi_r)_{\text{cr}}, (\vartheta_{\text{OK}})_{\text{cr}}, (\vartheta_r)_{\text{cr}}$ the same values in stoichiometrical mixture.*

*During calculation of stoichiometrical composition in gas mixtures, where "fuel" consists of one or more combustible gases (with $\vartheta_{r,i}$ parts by volume with respect to "fuel"), and "oxidizer" consists of active gas (for example, O_2) and inert diluents (for example, N_2) with $\vartheta_{\text{OK AKT}}, \vartheta_{\text{OK III}}$ parts by volume (with respect to "oxidizer"), it is possible to use the following formula:

Accordingly, for surplus of fuel $0 < \alpha < 1$, for stoichiometrical mixture $\alpha = 1$, for surplus of oxidizer $1 < \alpha < \infty$.

Let us note that in examining the question about position of maximum burning rate, it is possible to use both mass and linear burning rate with a practically identical result, because the density of a majority of gaseous and condensed mixtures changes comparatively little in a sufficiently wide interval α . The only exceptions are mixtures consisting of components with sharply different density (for example, $H_2 - O_2$ or $W - KClO_4$), where $m_{\max}$ can be noticeably shifted relative to $u_{\max}$ in the direction of greater percentage of heavy component.

We will now examine the position of maximum burning rate for gas mixtures.

For air mixture ($p = 1$ [atm(abs.)]), according to survey work [1], $u_{\max}$ lies near $\alpha = 1$: for some mixtures during a small surplus of fuel ($\alpha \geq 0.8$), for others during a small surplus of oxidizer ($\alpha \leq 1.12$). Exceptions are CO - air and H_2 - air mixtures, where $u_{\max}$ lies at considerable surplus of fuel (for example, for a CO - air mixture at $\alpha \approx 0.49$).

With decrease of dilution of mixture by inert component (in particular, during transition from air mixtures to oxygen mixtures, the maximum burning rate of mixtures with H_2 and CO base is displaced in the direction of stoichiometry. Thus, for example, according to John (quot. on [8]), during

[FOOTNOTE CONTINUED FROM PRECEDING PAGE].

$$(\theta_r)_{\text{crex}} = \{1 + (\sum_i k_{i, \text{ANT}} \theta'_r)_i / \theta'_{\text{OK, ANT}}\}^{-1}, \quad (1)$$

where $k_{i, \text{ANT}}$ is the number of moles of active component of oxidizer necessary for complete oxidation of one mole of the i -th fuel.

Thus, for example, for a H_2 - air mixture, $k_{H_2, \text{ANT}} = 0.5$, $\theta'_{H_2} = 1$ (hydrogen is taken without impurities), and $\theta'_{\text{OK, ANT}} = 0.2093$. Accordingly $(\theta_r)_{\text{crex}} = 0.293$. If there is inert gas in the composition of the fuel, then for it $k_{i, \text{ANT}} = 0$. If the oxidizer consists only of an active component, then $\theta'_{\text{OK, ANT}} = 1$. Accordingly, for mixtures the combustible gas (without impurities), O_2 of formula (1), is simplified:

$$\theta_r)_{\text{crex}} = (1 + k_{i, \text{ANT}})^{-1}. \quad (1')$$

change of oxygen content in composition of oxidizer of $x\%O_2 + (100 - x)\% N_2$ from $x = 21\%$ to $x = 98.5\%$ maximum burning rate for mixture with hydrogen shifts from $\alpha = 0.56$ to $\alpha = 0.78$, and for a mixture with carbon monoxide from $\alpha = 0.37$ to $\alpha = 0.62$. For mixtures with a benzene base [3], during a change of x from 16.4 to 88.6%, maximum burning rate is displaced from $\alpha = 0.74$ to $\alpha = 0.92$. For mixtures with a methane base (according to John), essential displacement of maximum is not observed (during change of x from 21 to 98.5%).

There are only separate works [2, 5, 7] where function $u(\alpha)$ has been studied at high pressures. Position $u_{\max}$ is established rather approximately (for example, in works [5, 7] step by α near $u_{\max}$ composed $\Delta\alpha \approx 0.1$). Taking into account the accuracy shown of determination of position of maximum, it is possible on the basis of works [2, 5, 7] to come to the conclusion that increase of pressure does not lead to considerable displacement of $u_{\max}$. Only for mixtures with a CO base according to increase of pressure is there noted [2] displacement of $u_{\max}$ in the direction of stoichiometry (Table 5).

Table 5. Displacement of Maximum Burning Rate with Increase of Pressure for Mixtures with a CO Base

Pressure in [atm (abs.)]	$u_{\max}$			Pressure in [atm (abs.)]	$\alpha_{u_{\max}}$	
	CO - O ₂	CO	air		CO - O ₂	CO - air
1	0.60	0.41		52	0.82	—
5.1	0.70	—		91	0.86	0.71
21.4	0.82	0.53				

Thus, for gaseous mixtures (in any case, if they are not too ballasted by inert component and if pressure is sufficiently great), the maximum burning rate lies near the stoichiometrical composition.

As mixture ratio deviates from $\alpha_{u_{\max}}$ (i.e., from the composition corresponding to maximum burning rate), curve $u(\alpha)$ drops at first rather hollow, and then all the more steeply (and finally at a certain α_{limit} , burning fades). The form of curve $u(\alpha)$ will be characterized by the ratio $u/u_{\max}$ at different $\alpha/\alpha_{u_{\max}}$.

Let us note two results obtained for gaseous mixtures.

1) From the present works [2, 3] and others, it follows that with decrease of content of inert diluent (in particular, during transition from air mixtures to oxygen mixtures) curves $u(\alpha)$ become more oblique. In other words, surplus of fuel or oxidizer in oxygen mixture has a weaker effect on burning rate than in an air mixture (Table 6).

Table 6. Lowering of Burning Rate of a Benzene +
[x% O₂ : (100-x)% N₂] Mixture Ratio from $\alpha_{u_{max}}$ at a
Different Pro-cent of Nitrogen [3] (p = 1
[atm(abs.)])

$\alpha_{u_{max}}$	u/u_{max}						
	x = 20,8	x = 21,4	x = 40,0	x = 51,5	x = 67,2	x = 83,3	x = 100
1,6	—	—	—	0,87	0,92	0,89	0,94
0,8	0,85	0,91	—	0,96	0,97	0,98	0,95
0,7	0,66	0,77	0,80	0,87	0,89	0,93	0,88
0,6	0,48	0,56	0,61	0,69	0,73	0,77	0,74
0,5	0,28	—	0,40	0,42	0,49	—	0,47

2) Value u/u_{max} can essentially depend on pressure [2]. For CO - O₂, CO - air, and CH₄ - O₂ mixtures at an α , sufficiently deviating from $\alpha_{u_{max}}$, there is observed an essential decrease, u/u_{max} , with increase of pressure. In other words, a surplus of components compresses burning rate more strongly at high pressures and more weakly at low pressures (Table 7).

Table 7. Lowering of Burning Rate of Gas Mixtures
According to Deflection of Mixture Ratio from
 $\alpha_{u_{max}}$ at Different Pressures [2]

Mixture	$\alpha_{u_{max}}$	u/u_{max}				
		p = 1 [atm (abs.)]	p = 5.1 [atm (abs.)]	p = 21.4 [atm (abs.)]	p = 52 [atm (abs.)]	p = 90 [atm (abs.)]
CO - O ₂	3,0	0,74	0,67	0,50	—	—
	2,5	0,80	0,76	0,61	—	—
	0,5	0,84	—	0,61	0,63	—
	0,4	0,77	—	0,42	0,42	—
CO - Air	1,6	0,86	—	0,74	—	0,51
	1,4	0,92	—	0,84	—	0,70
CH ₄ - O ₂	1,6	0,82	—	0,78	—	0,73
	0,6	0,72	—	0,32	—	0,41
	0,5	0,52	—	0,13	—	—

C. Burning Rate as a Function of Pressure

We will approximate a real curve $m(p)$ with an exponential function:

$$m = bp^v. \quad (2)$$

If range of pressure is wide, it is usually necessary to break it into several sections and find values b and v separately for every section. Nonetheless, application of formula (2) is justified because of its simplicity and convenience.

For all (unfortunately, not numerous) oxygen mixtures studied value v is close to one (Table 8) and does not reveal a systematic dependence on α . For a $H_2 - O_2$ mixture, index v is essentially larger than one [2]: in the interval of 14-90 [atm(abs.)], $v_{\alpha=1.33} \approx 1.42$; $v_{\alpha=0.46} \approx 1.56$.

For air mixtures, value v is in general, lower than for oxygen mixtures. For methane-air mixture, $v \approx 0.5$, although separate values sharply fall (see Table 8). For mixtures of propane, ethane, and ethylene with air [6], value v is noticeably higher ($v \approx 0.65-0.85$), and for C_2H_2 - air mixture [4], $v \approx 1$.

In a number of cases, index v essentially depends on pressure. For some mixtures, value v decreases during transition to higher pressures (see data in Table 8 for CH_4 - air mixture at $\alpha = 1.2$ and 0.90, and also data for CO - air mixture). Conversely, for other mixtures, value v increases during transition to high pressures (see data in Table 8 for $CH_4 - O_2$ at $\alpha = 0.75$ and 0.61).

For CO - air mixture there is observed a lowering of v with increase of fuel surplus (especially at high pressures, see Table 8). High v values are obtained for the flame of disintegration of acetylene ($v_{1-10 \text{ atm}} \approx 1.44$ [18]; $v_{2.5-5 \text{ atm}} \approx 2.1$ [19]) and propyne ($v_{10-19 \text{ atm}} \approx 1.06$ [18]).

Table 8. Value of Index v in Formula $m = bp^v$ for Certain Gas Mixtures (Figures in Parentheses are Pressure in atm)

Mixture	α	2.0	1.5	1.16	0.93	0.75	0.61
$CH_4 - O_2$ [2]	v	1.04 (1-90)	1.07 (1-90)	1.13 (1-90)	1.13 (1-90)	1.08 (1-21) 1.25 (21-90)	0.98 (1-21) 1.29 (21-90)
	α	3.0	2.0	1.33	0.86	0.5	
$CO - O_2$ [2]	v	1.06 (5-21)	1.15 (5-52)	1.10 (1-90)	1.08 (1-90)	1.04 (1-90)	
	α	1.2	1.1	1.0	0.95	0.90	0.80
CH_4 - Air	v	0.70 (1-21) [2] 0.54 (1-60) [5] 0.37 (21-90) [2]	0.54 (2-19) [7]	0.68 (1-20) [4] 0.48 (2-40) [7]	0.59 (1-21) [2] 0.52 (1-60) [5]	0.48 (2-19) [7] 0.53 (1-60) [5] 0.23 (19-40) [7]	0.22 (2-40) [7]
	α	0.98	0.78	0.63	0.51	0.42	0.34
CO - Air [2]	v	0.90 (1-21) 0.74 (21-90)	0.92 (1-21) 0.74 (21-90)	0.91 (1-21) 0.66 (21-90)	0.92 (1-21) 0.46 (21-90)	0.84 (1-21) 0.34 (21-90)	0.73 (1-21) 0.11 (21-90)

D. Burning Rate as a Function of Initial Temperature

With increase of initial temperature T_0 , mass (and, all the more so, linear) burning rate increases (Fig. 5).

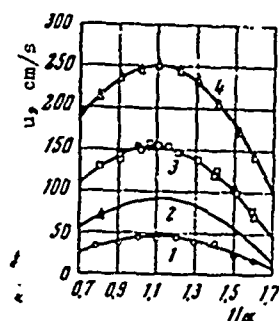


Fig. 5. Dependence of burning rate of C_3H_8 - air mixture on relationship of components at different initial temperatures ($p = 1$ [atm(abs.)]) [21].

1 - 311.0°K; 2 - 477.6°K; 3 - 644.3°K.
4 - 811.0°K.

The data of Passauer (quot. on [8]) are satisfactorily described by empirical formula:

$$m = b' T_0, \quad (3)$$

where T_0 is expressed in °K.

If, however, dependence of burning rate on temperature of flame T_f is used in the form:

$$m \sim e^{-E/RT_f}, \quad (4)$$

where E is activation energy in cal/mole, then in the absence of dissociation, function $m(T_0)$ will have the form:

$$m \sim e^{-E/R(T_0 + q\bar{c})}, \quad (4')$$

where q is heat of burning in cal/g; $\bar{c}$ is average heat capacity of products of reaction in cal/g·deg.

Besides formulas (3) and (4'), function $u(T_0)$ is also characterized by the ratio $u_{T_{01}}/u_{T_{02}}$ of burning rates at definite initial temperatures (for example, $u_{100^\circ}/u_{20^\circ}$), or by the coefficient:

$$\beta_u = \frac{1}{u} \frac{\partial u}{\partial T_0} = \frac{\partial \ln u}{\partial T_0}, \quad (5)$$

or by the analogous coefficient for mass burning rate:

$$\beta_m = \frac{1}{m} \frac{\partial m}{\partial T_0} = \frac{\partial \ln m}{\partial T_0}. \quad (6)$$

For condensed systems, β_u and β_m are similar among themselves, since dependence of density on initial temperature is weak (in many cases, it can be disregarded). For gas systems:

$$m = \rho \cdot u = \frac{p u}{RT_0} = \frac{p u}{R} \cdot \frac{1}{T_0}.$$

At $p = \text{const}$ we will obtain instead of (6):

$$\beta_m = \frac{\partial \ln u/T_0}{\partial T_0}. \quad (6')$$

Obviously, coefficients β_u and β_m themselves depend on initial temperature. Thus, if there occurs function $m(T_0)$ of type (3), then $\beta_m = 1/T_0$ (for example, at room temperature, $\beta_m \sim 3.4 \cdot 10^{-3} \text{ deg}^{-1}$, and at 500°C $\beta_m \sim 1.3 \cdot 10^{-3} \text{ deg}^{-1}$). If, however, there occurs (4'), then

$$\beta_m = E/2RT_0^2 = E/2R(T_0 + q/c)^2. \quad (7)$$

However, if the interval of change, T_0 is not too great, experimental points in coordinates $(\ln m, T_0)$ or $(\ln u/T_0, T_0)$ in many cases satisfactorily descend on a straight line, the slope of which gives a mean value β_m in a given interval, T_0 . In Table 9 there are given values β_m defined in such a way for a number of air mixtures at atmospheric pressure.

From Table 9 it is clear that for stoichiometrical mixtures of H_2 , CH_4 , C_3H_8 , C_6H_6 , $n\text{-C}_7\text{H}_{16}$, $\text{iso-C}_8\text{H}_{18}$ with air, values β_m are close to $2 \cdot 10^{-3} \text{ deg}^{-1}$ and differ little among themselves. Let us note that combustion temperatures of stoichiometrical mixtures of H_2 , CH_4 , C_3H_8 , C_6H_6 differ little among themselves and are close to $2200\text{-}2300^\circ\text{K}$ (see Table 1).*

According to increase of initial temperature, β_m decreases in agreement with (7) or with function $\beta \sim 1/T_0$ (which follows from (3)). This effect is especially noted for rich mixtures.

Finally, for mixtures given in Table 9, there appears fully distinctly the effect noted for the first time by G. V. Lukasheney: during change of α (i.e., during change of mixture ratio), temperature coefficient β_m passes through a minimum, which lies approximately in the same place where the maximum burning rate lies (Fig. 6).

*If from (7) to calculate value of activation energy, then we will obtain (during $\alpha = 1$):

Combustible gas (+ air).....	H_2	CH_4	C_6H_6
E, kcal/mole.....	44	38.5	34.8

Table 9. Value of Temperature Coefficient of Burning Rate $\beta_m = \frac{\partial \ln m}{\partial T_0}$ for a Series of Air Mixtures at Atmospheric Pressure

α	$\beta_m \cdot 10^3$				
	Data of Passauer (see [8])		Present works [21]	Present works [22]	
	hydrogen*	methane	propane**	benzene	n-heptane isooctane
1.43			2.09 (38-538°C)		
1.18		2.46 *** (20-520°C)			
1.11			1.70 (38-538°C)	1.64 (25-427°C)	1.74 (25-434°C)
1.05		2.08 *** (20-520°C)			
1.0	2.01 (20-430°C)			1.60 (25-427°C)	1.78 (35-306°C) 1.53 (140-434°C)
0.94		1.90 *** (20-520°C)			
0.91			1.51 (38-538°C)	1.72 (25-427°C)	1.69 (35-306°C) 1.65 (25-434°C)
0.88		1.62 [5] (16-220°C)			
0.86		1.90 *** (95-520°C)			
0.79		3.76 (95-350°C)			
		0.96 (350-680°C)			
0.77			1.56 (38-538°C)		
0.74	1.99 (190-430°C)	1.07 (350-610°C)			
0.68		2.13 (350-520°C)	1.90 (38-538°C)		

*At $\alpha = 1.48; 0.59; 0.49$ and 0.42 , β_m continuously decreases with increase of T_0 .

**At $\alpha = 0.59$, β_m continuously decreases with increase of T_0 in the interval $205-538^\circ\text{C}$.

***In interval $520-680^\circ\text{C}$ β_m decreases.

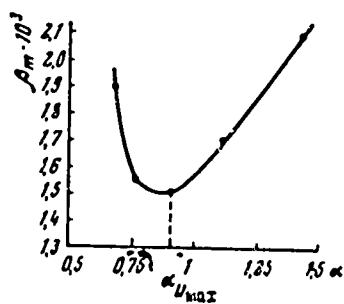


Fig. 6. Dependence of temperature coefficient $\beta_m = d \ln m / d T_0$ deg⁻¹ on relationship of components α for C_3H_8 - air mixture [21]. The vertical broken line shows the position of maximum burning rate.

E. Influence of Small Additions on Burning Rate

There is a series of works, where it is experimentally shown that with the help of small additions (gaseous or in the form of finely divided solid particles), it is possible to essentially affect burning rate in homogeneous gas mixtures.

The best known example is the burning of carbon monoxide. Thoroughly dried CO - O₂ mixtures, in general, do not ignite. However, during addition of a small quantity of vapors of water (design heat of burning only descends), the mixture becomes combustible where burning rate increases with increase (up to definite limits) of percentage of water. Thus, in work [23] there are given the following data of Bon for a mixture of 45% CO + 55% air:

Water vapor, %.....	0.7	1.45	3.5	5.2	8.0
u, cm/s.....	56	76	106	120	118

In work [24] there is investigated the action of a large number of gaseous additions on the burning rate of a H₂ - air mixture. Table 10 gives corresponding data for burning rate, and also for value $Z = u_c \text{ доб} / u \text{ без доб}$, is the burning rate of the initial mixture; $u_c \text{ доб}$ is the burning rate of the mixture with the addition.

Besides compounds enumerated at the beginning of Table 10, burning rate is rather effectively lowered by additions of acetylene and ammonia. Conversely, additions of SO₂, SF₆, NO, NCl, SiF₄, CO₂, BF₃, CO, NO₂, ClF₃, N₂O, and Cl₂ lowered burning rate insignificantly.

Table 10. Influence of Different Gaseous Additions on the Burning Rate of a H₂ - Air Mixture at $\alpha \approx 0.7$.
Content of Addition is 2% by Volume; p = 1 [atm(abs.)]
T₀ = 25°C

Addition	u, cm/s	Z	Addition	u, cm/s	Z
Without addition . . .	200	—	1,1-Difluorethane . . .	135	0,45
1,3 Butadiene	27	0,09	Methane	144	0,48
n-Butane	46	0,15	Methylbromide	154	0,51
Dibromtetrafluorethane	54	0,18	Methylchloride	199	0,66
Ethylchloride	80	0,27	1,1 difluorethylene .	202	0,67
Ethylene	100	0,33	Vinyl chloride	230	0,77

Out of a number of additions of vapors of different liquids burning rate was effectively lowered by aniline, benzene, ethyl ether, pentacarbonyl of iron, toluene, n-octane, and acetone; burning rate was insignificantly lowered by acetic acid, nitromethane, tetraethyl lead, chloroform, and carbon tetrachloride. Water vapors increased burning rate.

In work [25] there is investigated the lowering of the burning rate of a stoichiometrical mixture of methane with air during addition of certain finely pulverized salts (Table 11).

Table 11. Influence of Additions of Certain Powders on Burning Rate of CH_4 - Air Mixture at $\alpha = 1$ at Atmospheric Pressure

Addition	Specific surface of addition, cm^2/g	Concentration of addition, mg/cm^3	u , cm/s	z
Without addition	—	—	6.5	—
Na_2CO_3	10800	0,01	17	0,26
	4940	0,01	17	0,26
	10800	0,02	13,8	0,21
	4940	0,02	13,8	0,21
NaHCO_3	11900	0,01	13	0,23
	7760	0,01	55	0,85
	11900	0,02	14	0,22
	7760	0,02	26	0,40
	11900	0,04	13	0,20
	7760	0,04	13	0,20
KHCO_3	12400	0,01	14	0,22
NaCl	4500	0,01	31	0,48
	4500	0,02	18	0,28
CaCl_2	3000	0,01	34	0,52
	3000	0,02	22	0,34
	3000	0,04	15,5	0,24
K_2SO_4	5200	0,01	16	0,25

It is noted that the action of addition of NaHCO_3 on a C_3H - air mixture and especially on an NH_3 - O_2 - N_2 mixture is much weaker than on a CH_4 - air mixture.

F. The Theory of Propagation of a Flame in Homogeneous Systems

We have already noted that burning rate in homogeneous systems depends on speed of chemical reactions in front of burning and on speed of transmission

of heat and active particles from front of burning to fresh mixture.

The problem of finding burning rate requires joint solution of equations of chemical kinetics, diffusion, and thermal conduction.

There is a large number of works where there has been conducted either a numerical solution of this system of equations for burning of concrete mixture, or an approximate solution, which not infrequently permits obtaining a comparatively simple expression for the burning rate of a definite class of mixtures.

Among approximate theories there are usually isolated the thermal and diffusion theories.

The thermal theory of burning can be used during different mechanisms of reaction in flame, if only there is observed similarity of fields of temperatures and concentrations. Diffusion theory is used during chain mechanism of reaction in flame, especially in those cases, when concentration of hydrogen atoms in zone of reaction is great.

We will stop only briefly on approximate thermal theory of burning, since for condensed systems, which interest us in the present work, there were made only single attempts [240] to use approximate diffusion theory* or numerical methods of solution of full system of equations of burning because of the absence of information about mechanism of reactions in flame.

Out of the number of approximate thermal theories of burning, the most widely used is a theory which was developed at the end of the thirties and in the beginning of the forties at the Institute of chemical physics of the Academy of Sciences of the USSR by Ya. B. Zel'dovich and D. A. Frank-Kamenetskiy with the closet creative participation of N. N. Semenov (see [26, 28, 192, 193]) in reference to burning of gases and was then extended to burning of volatile explosives (see [46], and also [27]).

In this theory it is accepted that speed of reaction increases exponentially with temperature, and burning occurs in one narrow zone in the gas phase.** Practically all heat emission is concentrated in a narrow interval of temperatures (on the order of RT_p^2/E wide) near the maximum combustion temperature.

According to this theory the expression for burning rate can be recorded in the simplest form thus:

$$m \sim \sqrt{\frac{2k\phi_{max}}{q^2} \frac{RT_p^2}{E}} \sqrt{\frac{2k\phi_{max}}{[c(T_p - T_0)]^2} \frac{RT_p^2}{E}} \quad (8)$$

*Qualitative considerations about possible influence of diffusion of active gaseous products during burning of ammonium perchlorate are contained in works [106, 107].

**With considerable limitations, this theory can also be used for so-called flameless burning, when the reaction takes place completely in one narrow zone in the condensed phase.

where λ is the coefficient of thermal conduction of mixture flowing into the zone of reaction, cal/cm·s·deg; $\dot{q}_{\max}$ is speed of liberation of heat in a unit of volume of the zone of reaction at $T \sim T_r$, cal/cm³·s; q is heat of reaction, cal/g; $\bar{c}$ is average heat capacity, cal/g·deg.

In the theory it is accepted that $\phi_{\max} \sim e^{-E/RT_r}$. Regarding dependence on concentration C of substance (and for systems reacting in the gas phase, — and thereby on pressure), for the case of a simple reaction of the n -th order, $\phi_{\max} \sim C^n$. Hence will obtain approximately:*

$$m \sim p^{n/2} e^{-E/2RT_r} . \quad (9)$$

In case of more complete output:

$$m \sim p^{n/2} \left(\frac{T_0}{T_r} \right)^{n/2} \left(-\frac{RT_r^2}{E} \right)^{(n+1)/2} (T_r - T_0)^{-(n+1)/2} e^{-E/2RT_r} . \quad (10)$$

In literature there is a number of works where an attempt has been made to find the connection between burning rate and combustion temperature. Combustion temperature was changed at the expense of: 1) transition from one mixture to another; 2) dilution of mixture by inert component (for example, nitrogen) or surplus of fuel or oxidizer; 3) change of initial temperature of mixture; 4) heat removal from zone of burning with the help of cooled burner.

In first case, a simple connection between temperature and burning rate is not revealed, which, however, is naturally, if one originates from formulas (9) and (10), since value of activation energy can change during transition from one mixture to another. Nonetheless, it turned out [9] that for definite groups of mixtures, function $u(T_r)$ is the same (for example, on the same curve there lie points for a series of hydrocarbons, alcohols, and esters in a mixture with O_2 and N_2 ; however, this curve is not plotted according to formulas (9) and (10)).

In works [21, 22], combustion temperature changed at the expense of change of initial temperature. Function $u(T_r)$ will agree with formulas (9) and (10). Values of activation energy for air mixtures of benzene, n-heptane and isooctane, according to [22], are similar among themselves (Table 12).

In work [29], combustion temperature changed at the expense of heat withdrawal from flame to cooled burner. In the region of 1300-1900°K in coordinates $\ln u$, $1/T_r$, experimental points lay well in a straight line, the slope of which (i.e., value of activation energy) weakly depends on α (with the exception of CH_4 — air mixture) and is approximately the same for air mixtures of acetylene, ethane, propane, and hydrogen.

*In a number of cases, combustion temperature depends on pressure (for example, at sufficiently high T_r when dissociation becomes essential, combustion temperature increases somewhat according to increase of pressure). This circumstance must be considered in examining function $m(p)$.

Table 12. Value of Activation Energy During Burning of Stoichiometrical Air Mixtures at Atmospheric Pressure

Combustible gas	E, kcal/mole				Combustible gas	E, kcal/mole			
	[10]	[24]	[25]	[29]		[10]	[24]	[25]	[29]
Hydrogen	16	--	--	47	Propane	26	33,1	--	53
Acetylene	20	--	--	47	Benzene	27	--	43	--
Ethylene	24	--	--	50	n-Heptane	--	--	34	--
Methane	26	--	--	65	Isooctane	--	--	39	--
Ethane	26	--	--	50					

*Data for mixtures with $u_{\max}$ (however, $\alpha_{u_{\max}} = 0.95-0.97$, i.e., is close to $\alpha = 1$).

Authors of enumerated works emphasize that due to the complexity of mechanism of reactions in the flame, the value of activation energy should be examined as a certain total characteristic. It is not remarkable, therefore, that the numerical value of activation energy for a given mixture can strongly depend on the method of determination. In Table 12 there are given values of activation energy which were calculated by proceeding from function $u(T_F)$, and also taken from work [10], where they were determined from the relationship between activation energy and combustion temperature on poor limit. It is necessary to note that for a majority of combustible gases (in mixtures with air) investigated in work [10], value of activation energy lies in comparatively narrow limits — from 25 to 30 kcal/mole. Considerable deflections are observed only for carbon bisulfide (16 kcal/mole), hydrogen (16 kcal/mole) and acetylene (20 kcal/mole).

Divergence between the data of works [10] and [29] is extraordinarily great.

It is necessary to consider that the values of activation energy in work [29] pertain to an interval of temperatures of 1300-1900°K. It is possible that during adiabatic combustion temperature (2200-2500°K for given mixtures), the value of activation energy would be lower. Apparently, the usual interval should be considered 30-40 kcal/mole.

It is of interest to estimate order of magnitude for speed of liberation of heat ($\phi_{\max}$) in zone of burning. Such an appraisal is useful during comparison of different types of flames and especially in examining flames, where there simultaneously occurs burning of homogeneous mixture and solid particles (see below). Unfortunately, measurement of $\phi_{\max}$ (by profile of temperatures) is combined with great difficulties and errors and is practically carried out only at low pressures. The order of magnitude of $\phi_{\max}$ can also be estimated by using (8) and relationships analogous to it.

For mixtures of hydrocarbons with air, such appraisals are collected in work [30]. At atmospheric pressure, the most probable estimate is about 10^3 cal/cm³·s. Let us note that the appraisal according to (8) is:

$$\Phi_{\max} \approx \frac{m^2 [\bar{c}(T_F - T_0)]^2}{2\lambda} \cdot \frac{E}{RT_F^2} \quad (11)$$

at $m = 0.05 \text{ g/cm}^2 \cdot \text{s}$; $\bar{c} = 0.3 \text{ cal/g} \cdot \text{deg}$; $T_F = 2300^\circ \text{K}$; $T_0 = 300^\circ \text{K}$; $\lambda = 4 \cdot 10^{-4} \text{ cal/cm} \cdot \text{s} \cdot \text{deg}$ and $E = 3 \cdot 10^4 \text{ cal/mole}$ gives $\Phi_{\max} \approx 3 \cdot 10^3 \text{ cal/cm}^3 \cdot \text{s}$, i.e., three times higher than according to work [30].

For oxygen mixtures at atmospheric pressure, $m = 0.1-0.5 \text{ g/cm}^2 \cdot \text{s}$ (see Table 1). Taking $T_F = 3000^\circ \text{K}$, we will obtain from (11) $\Phi_{\max} = 1.5 \cdot 10^4 - 3.5 \cdot 10^5 \text{ cal/cm}^3 \cdot \text{s}$. In work [12] for $\text{C}_2\text{H}_4 - \text{O}_2$ mixture, there is given a speed of oxygen intake in zone of reaction of about $4 \text{ moles/cm}^3 \cdot \text{s}$, which gives for $\Phi_{\max}$ a value on the order of $10^5 \text{ cal/cm}^3 \cdot \text{s}$.

During increase of burning rate at the expense of increase of pressure, $\Phi_{\max}$ increases proportionally to the square of burning rate [see (11)]. Accordingly, at $100[\text{atm(abs.)}]$, when for oxygen mixtures of hydrogen and methane, mass burning rate is on the order of $10^2 \text{ g/cm}^2 \cdot \text{s}$, value $\Phi_{\max}$ becomes on the order of $10^{10} \text{ cal/cm}^3 \cdot \text{s}$.

§ 2. Burning of Volatile Explosive Substances

Burning of volatile explosives [VV] (BB) occurs in gas phase above surface of charge and, therefore, should obey the same regularities, as the burning of homogeneous gas mixtures.

Actually, the earliest and at the same time, the most complete and sufficiently successful comparison of the approximate thermal theory of Ya. B. Zel'dovich and D. A. Frank-Kamenetskiy (see above) with experiment was carried out not for gas mixtures, but for volatile VV — nitroglycol, $\text{O}_2\text{NOCH}_2\text{CH}_2\text{ONO}_2$ [31].

Absolute value of burning rate of volatile VV and its dependence on pressure and initial temperature are close to analogous dependences for gas systems.

At the same time, it is necessary from the very beginning to emphasize the distinction between burning of explosives and burning of gas systems. These distinctions first of all concern stability of front of burning.

During burning of gas mixture on a burner, appearance of disturbances of front of burning is combined with appearance of turbulence in flow of fresh mixture.

Accordingly, the condition of stability of a laminar flame coincides with the condition of stability of laminar flow in a pipe, i.e., with condition

$\text{Re} = \frac{Rv\rho}{\eta} \leq \text{Re}_{\text{кр}}$ (where R is radius of pipe; ρ is density of gas; η is dynamic viscosity of gas, $\text{g/cm} \cdot \text{s}$). Presence of burning can only somewhat change

value Re_{kp} (as compared to flow without burning). In examining the process of development of disturbances, there can be attracted results accumulated in the theory of turbulence. The question about stability of burning a gas mixture in a pipe or spheric bomb is more complex. Here, in particular, one should consider the effect of autoagitation of the flat flame front predicted theoretically by L. D. Landau [32]. However, in usual conditions of carrying out experiments the effect of autoagitation of a gas flame, apparently cannot be developed.

Conversely, during burning of liquid VV the effect of autoagitation* appears very easily, so that laminar** burning of liquid VV can be observed only at sufficiently low pressures.

According to [33], burning of liquid VV is stable only at $m < m_{kp}$, where

$$m_{kp} = \sqrt{\frac{4\alpha' g \rho_l^2 \rho_g^2}{\rho_l - \rho_g}} \quad (12)$$

Here α' is surface tension of liquid (at that temperature, which is attained on surface of burning liquid), dynes/cm; g is acceleration of gravity, cm/s^2 ; ρ_l , ρ_g are densities of liquid and gaseous products of its burning.

Applicability of formula (12) as a criterion of stability of burning of liquid VV was investigated in detail by K. K. Andreyev. The values of m for methyl nitrate $H_3C - O - NO_2$ calculated by him from (12) turned out to be

equal to $0.32 \text{ g/cm}^2 \cdot s$, for nitroglycol they turned out to be $0.88 \text{ g/cm}^2 \cdot s$. Experimental values of m_{kp} for methyl nitrate lie between 0.26 and $0.46 \text{ g/cm}^2 \cdot s$ (near 1.75 [atm(abs.)]), for nitroglycol they lie near $0.90 \text{ g/cm}^2 \cdot s$ (near 20 atm) [35]. Transition to disturbed burning is accompanied by amplification of function $u(p)$ [36, 37].

*This effect was also predicted by L. D. Landau [33] and in a somewhat other setting was examined by V. G. Levich [53]. In work [34] there are examined certain investigations from the theory of L. D. Landau.

**In the region of burning of condensed systems up to now, there is no stabilized terminology for designation of undisturbed and disturbed burning. In the first case there are used the terms "stationary burning," "stable burning," "normal propagation of flame," "layer by layer burning"; in the second there are used the terms "nonstationary burning," "unstable burning," "turbulent burning," "disturbed burning," "convection burning," etc. To describe transition from the first conditions of burning to the second there are used the terms "disturbance (or breakdown) of stable conditions of burning," "breakthrough burning," "penetration of burning in depth of charge," etc.

For solid VV, breakdown of laminar burning (at a certain critical pressure p_{kp}) is combined with penetration of gaseous products of burning into pores of fresh substance (see [35, 198, 199, 230] and others). Value p_{kp} decreases with increase of porosity of charge, and at a porosity, it decreases in proportion to increase of crystals of substance (since diameter of pores increases, although their number decreases). The presence of a liquid layer on the surface of a charge promotes increase of p_{kp} . If VV can crack in the course of burning (under the influence of temperature stresses [40]), breakdown of laminar burning can occur in those cases, when the cold substance was monolithic [43]. A trivial cause of breakdown of laminar burning can be penetration of products into clearance (even the most insignificant one if only there is one) between charge and shell* [38].

A. Absolute Value of Burning Rate

The number of works dedicated to VV burning is considerably less than for gas systems. However, if for gas systems almost all data are obtained at $p \leq 1$ [atm(abs.)], then for condensed systems almost all works pertain to raised pressures, but part of the works is carried out at pressures up to 1000-10,000 atm. This is combined first of all with demands of practice (for ballistite powders utilized in trunk systems, operating pressure is on the order of 10^3 atm; for solid rocket propellants, operating pressure is on the order several tens of atmospheres; high pressures can be developed during ignition of VV in different shells, etc.). Furthermore, from a methodical point of view, it is much easier to work with condensed systems at high pressures than it is to work with gas.

Table 13 gives data on the burning rate of a number of volatile explosives.

All these substances are contained in a molecule of group NO_2 . According to existing ideas, during disintegration of a VV molecule there occurs splitting of groups NO_2 with subsequent reaction between NO_2 and hydrocarbon fragments of the molecule.

It is natural, therefore, to expect that the mass burning rate of volatile VV will be close to the mass burning rate of gas mixtures with an NO_2 base.

Actually, at atmospheric pressure, there is such correspondence (see Tables 2 and 13). At high pressures in the case of gas mixtures, there are data only for H_2 - NO mixture (see Table 4).

Besides correspondence between speeds of burning (at atmospheric pressure), similarity between volatile VV containing NO_2 groups and gas mixtures based on oxides of nitrogen is expressed in the presence of two zones of burning. In division A § 1 it was noted that in the first zone of flame of gas mixtures on

*The necessity of using a shell (or plastering) is combined with the purpose that along a free (bordering on gas) surface of charge, a flame can spread with a speed significantly exceeding normal burning rate. This is combined with flowing around of charge by gaseous products of its burning [38, 39].

Table 13. Mass Burning Rate of Volatile Explosives

Substance	$m, \text{g/cm}^2 \cdot \text{s}$						
	1 [atm (abs.)]	10 atm	40 atm	100 atm	200 atm	400 atm	1000 atm
Methyl nitrate [35] CH_3ONO_2	0.143						
Nitroglycol [35] $\text{O}_2\text{NOCH}_2\text{CH}_2\text{ONO}_2$	0.042	0.392					
Hexogen [42]* $(\text{CH}_2\text{NNO}_2)_3$	0.061 **			3.06	5.22	9.54	22.5
PETN $\text{C}(\text{CH}_2\text{ONO}_2)_4$			0.77 [42] 0.80 [201]	1.93 [42] 1.95 [201]	3.86 [42]	7.72 [42]	18 [44]
Tetral [42]* $\text{C}_6\text{H}_2(\text{NO}_2)_3\text{NNO}_2\text{CH}_3$	0.067 [35]	0.312	0.815	1.55	2.49	4.60	11.4
Dyme [42]* $\text{O}_2\text{NN}(\text{CH}_2\text{CH}_2\text{ONO}_2)_2$	0.051		0.478	1.02			
Picric acid [42]* $\text{C}_6\text{H}_2(\text{NO}_2)_3\text{OH}$			0.46	0.945	1.75	3.36	8.19
Trotyl [42]* $\text{C}_6\text{H}_2(\text{NO}_2)_3\text{CH}_3$			0.326	0.756	1.47	2.90	7.29 6.65 [44]

*The values of m were calculated by empirical formulas given in work [42].

**Our data.

an NO_2 base, there occurs disintegration, $\text{NO}_2 \rightarrow \text{NO} + 0.5\text{O}_2$, and reaction of oxygen with fuel, but in second zone, there occurs reaction of NO with fuel. An analogous phenomenon is observed during burning of VV containing NO_2 groups. The distance Δ between the first and second zones can be considerable (for example, for nitroglycol at 12 atm, it is $\Delta \approx 1.8 \text{ cm}$ [37]).

With increase of pressure, Δ rapidly decreases. On photographs the first flame has the form of a narrow, weakly luminescent line; the second flame is very bright.

The question of multistage burning will be examined in § 10; here we will note only that if the distance between neighboring zones is great (millimeters or, all the more so, centimeters), burning rate is practically influenced only by the first zone of reaction, which is nearest to fresh substance. Accordingly, if one were to look for a connection between burning rate and combustion temperature, then it would make no sense to take final (equilibrium) combustion temperature. Here there inevitably appears the idea of effective combustion temperature T_{eff} [45, 47].

In work [47] there is given an appraisal T_{eff} of two different methods:

1) T_{eff} is calculated by formula (7) (at $T_r = T_{\text{eff}}$), proceeding from experimental value of temperature coefficient β and hypothetical value of activation energy $E = 37$ kcal/mole (this value is selected on the basis of data on slow thermal decomposition, and also data on binding energy $\text{RO} - \text{NO}_2$);

2) T_{eff} is measured with the help of a thermocouple (for value T_{eff} is accepted that temperature at which there is observed on the oscillogram a plateau (Fig. 7) or essential bend).

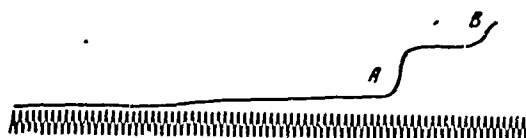


Fig. 7. Profile of temperature in zone of burning of nitroglycol at $p = 5$ [atm(abs.)] (thermocouple $W + 5\%$ $\text{Re} - W + 20\%$ Re ; $\varnothing 30 \mu$) [47]; Section A — first flame; section B — second flame.

In work [47] (and in work [42]) there is also given an approximate value of equilibrium combustion temperature T_p . In this case the approximate character of appraisal T_{eff} and calculation T_p does not have specific value, since we are interested only in the fact that value T_{eff} is considerably lower than T_p (Table 14).

Table 14. Value of Equilibrium and Effective Combustion Temperature for a Series of Volatile Explosives

explosive	p, atm	$T_{\text{eff}}, ^\circ\text{K}$ [47]		$T_p, ^\circ\text{K}$ [47]
		calculated by formula (15)	experiment (thermocouple)	
Nitroglycol	1	1300	1400	3100
	5	—	1600	3400
Tetryl	1	1470	1400	2800
	5	—	1500	2800
	10	—	1600	2800
	20	1630	—	2800
Nitroglycerine (gelated)	1	1350	—	3300
Methyl nitrate	1	1180	—	3200
Hexogene	1	1700	—	3300

It is another matter that for substances with high equilibrium (thermodynamic) combustion temperature, value T_{eff} can also be higher than T_{eff} for substances with low T_p . Therefore, there can be observed correspondence between burning rate and equilibrium combustion temperature. Such correspondence is noted in work [42] in the series trotyl-picric acid - tetryl - hexogene, but data for PETN and dyne fall out of this series (Table 15). However, calculation of activation energy carried out by formula (10) in assumption $T_r = T_p$ gives for a number of substances excessive values of 100-150 kcal/mole instead of the usual 30-50 kcal/mole [35].

Table 15. Burning Rate and Equilibrium Combustion Temperature for Certain Volatile Explosives

Explosive	$T_p, ^\circ\text{K}$	$\frac{m}{s/\text{cm}^2 \cdot s}$ (100 atm)	Explosive	$T_p, ^\circ\text{K}$	$\frac{m}{s/\text{cm}^2 \cdot s}$ (100 atm)
Trotyl	1980	0,756	Dyne	3000	1,02
Picric acid	2475	0,945	Hexogene	3500	3,06
Tetryl	2775	1,55	PETN	3800	1,93

It is possible that for gas mixtures based on oxides of nitrogen, non-correspondence between burning rate and equilibrium combustion temperature is combined with the fact that the second (high-temperature) zone weakly affects burning rate.

B. Dependence of Burning Rate on Pressure

For all volatile explosives (VV) studied, burning rate monotonously increases with increase of pressure. For a majority of volatile VV, function $u(p)$ is close to a direct proportion (Table 16).

For condensed systems, just as for gas mixtures, real curve $m(p)$ or $u(p)$ is frequently approximated with the help of exponential function:

$$m = \rho u \sim u = bp^v \quad (2)$$

(where $\rho \neq f(p)$ is the density of the initial condensed system). However, in literature it is also not infrequent to use binomial formulas of the form:

$$u = a + bp, \quad (2')$$

$$u = a + bp^v. \quad (2'')$$

Obviously, formulas (2) and (2') are special cases of formula (2'') (at $a = 0$ or at $v = 1$, respectively).

Certainly, in principle, binomial formulas (2') and (2'') can approximate experimental data in a wider range of pressure than corresponding monomial ($a = 0$) formula (compare, for example, No. 13 and 14, 15, and also 16 and 17, Table 16). Nonetheless, it is considerably more expedient to use monomial formula (2) (splitting the whole range of pressure into the necessary number of sections),

Table 16. Dependence of Burning Rate of Volatile Explosives on Pressure

No.	Substance	$\delta = \frac{p}{p_{\max}}$	Coefficients in formula $m(g/cm^2 \cdot s) = a + b p_{(atm)}^v$			Pressure, atm	Literature
			a	b	v		
1	Methyl nitrate ($\rho_{\max} = 1,21 g/cm^3$)	1,0	0,01	0,133	1,0	0,175-2,0	[35]
2			—	0,141	0,93	0,5-1,5	[35] *
3	Nitroglycol ($\rho_{\max} = 1,50 g/cm^3$)	1,0	0,0025	0,039	1,0	1-12	[35]
4			—	0,0415	0,97	1-12	[35] *
5	PETN ($\rho_{\max} = 1,77 g/cm^3$)	~1,0	—	0,0193	1,0	15-750	[42]
6		0,98	—	0,028	0,96	15-100	[43]
7			—	0,0173	1,0	500-1500	[44]
8	Dyne ($\rho_{\max} = 1,67 g/cm^3$)	~1,0	0,118	0,009	1,0	20-100	[42]
9			—	0,034	0,74	20-100	[42] *
10	Hexogene ($\rho_{\max} = 1,80 g/cm^3$)	~1,0	0,9	0,0216	1,0	100-1000	[42]
11			—	0,072	0,82	10-1000	[42] *
12	Octogene	0,875	—	0,0436	0,80	12-205	[200] *
13	Picric acid ($\rho_{\max} = 1,81 g/cm^3$)	~1,0	0,14	0,008	1,0	25-950	[42]
14			—	0,036	0,68	25-90	[42] *
15			—	0,0101	0,97	80-950	[42] *
16	Trotyl ($\rho_{\max} = 1,66 g/cm^3$)	~1,0	0,6	0,00716	1,0	20-950	[42]
17			—	0,022	0,75	35-100	[42] *
18			—	0,007	1,0	100-950	[42] *
19		0,98	—	0,025	0,77	28-105	[43]
20			—	0,0065	1,0	500-4000	[44]

*Coefficients in formula $m = b p^v$ have been calculated by us from experimental data of the work cited.

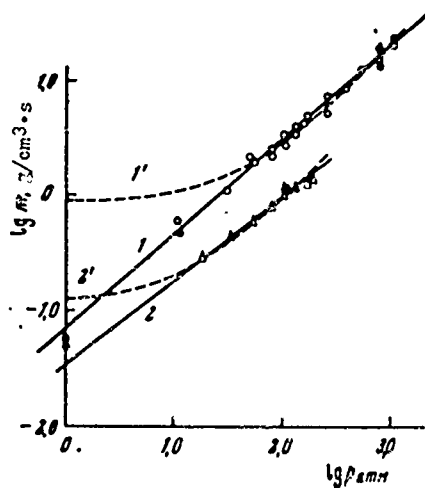


Fig. 8. Function $m(g/cm^2 \cdot s) = f(p_{atm})$ for hexogene (o) and dyne (Δ) [42]. 1 - straight line $m = 0.072p^{0.82}$, 1' - curve $m = 0.9 + 0.0216p$; 2 - straight line $m = 0.034p^{0.74}$; 2' - curve $m = 0.118 + 0.009p$. The traced point is our data at $p = 1$ [atm(abs.)].

since exactly such an appearance of function $u(p)$ follows from the theory of Zel'dovich — Frank-Kamenetskiy. Furthermore, in § 15 we will see that during calculation of pressure in combustion chamber of engine on solid fuel, only formula (2) is convenient. Moreover, analysis of source material shows that in certain cases binomial formulas (2') and (2'') were used without sufficient bases, and the same experimental data can be approximated with the same accuracy by monomial formula (2) in the same (or an even wider) range of pressures. Thus, for example, on Fig. 8, where in coordinates ($\lg m$, $\lg p$) there are plotted experimental points for hexogene and dyne [42], the solid straight lines, plotted from formula (2) considerably better approximate data at low pressures (including $p = 1$ [atm(abs.)]) than dash curves plotted from binomial formula (2'), which was used in work [42].

Data given in Table 16 show that at high pressures ($>100-200$ atm), the value of index ν (in formula $u = bp^\nu$) lies very close to one (only for hexogene $\nu \approx 0.82$). Let us remember that for oxygen gas mixtures, and also $H_2 - NO$ mixture (see § 1B) value ν is also close to one. This coincidence is hardly accidental. Presence of function $m \sim p$ is usually considered as a serious argument in favor of the idea that the leading reaction in the zone of burning is bimolecular.

However, for picric acid, trotyl, and also tetryl, function $u(p)$ is very close to a direct proportion in the region of high pressures, and it essentially weakens at "average" pressures (for tetryl at 200-950 atm, $\nu = 1$, and at 10-200 atm, $\nu \approx 0.7$). In other words, if at high pressures burning rate quickly drops with decrease of pressure, then at "average" pressures it starts to drop more slowly, and experimental points lie higher and higher above the straight line, $m = bp$ (responding to high pressures). Such an increase (relative to straight line $m = bp$) of burning rate is possibly connected with the effect studied in work [201]. This work showed that addition of 5% finely pulverized charcoal noticeably increases burning rate of PETN at 12-80 atm (the more, the lower the pressure). Index ν accordingly decreases (for pure PETN $\nu = 0.95$; for PETN with 5% charcoal, $\nu = 0.60-0.65$). Meanwhile, during burning of explosives with a large surplus of fuel (especially trotyl), in the zone of burning there will be formed a great deal of soot, which, possibly, leads to the same effect.

C. Dependence of Burning Rate on Initial Temperature

With increase of initial temperature T_0 , burning rate of condensed VV monotonically increases. Thus, as for gas mixtures, function $u(T_0)$ or $m(T_0)$ can be characterized by the formula:*

$$u \sim m \sim e^{-E/2RT_0}, \quad (13)$$

*For a majority of VV, function $\rho(T)$ is not determined, but there are no bases to consider that it is stronger than for ordinary solid or liquid substances (expansion coefficient of solids is $\sim 10^{-4} \text{ deg}^{-1}$; of liquids it is $\sim 10^{-3} \text{ deg}^{-1}$). Therefore, in the interval of temperatures 0-100-200°C, it is possible to take $\rho = \text{const}$, and then temperature coefficient for linear and mass burning rate will be the same.

where $T_r = f(T_0)$. For condensed VV, usually $T_r = T_{\text{exp}} < T_p$ (see section A of this paragraph), and therefore the form of function $T_r = f(T_0)$ cannot be established from general considerations.

This difficulty does not appear if one uses function u directly from T_0 (however such a function, naturally, no longer has that clear physical meaning which function (13) does). Thus, in work [35] there is used a function of the form:

$$1/u = a - bT_0. \quad (14)$$

Function $u(T_0)$ is also characterized by relation of burning rates $u_{T_{02}}/u_{T_{01}}$ at definite initial temperatures, and also temperature coefficient $\beta_u = d \ln u / dT_0 \approx \beta_m = d \ln m / dT_0$.

In small intervals experimental points are frequently grouped with identical success near straight line and in coordinates $1/u; T_0$ (as this requires (14)) and in coordinates $\lg u; T_0$ (which corresponds to definite constant value $\beta = d \ln u / dT_0$ (Fig. 9)).

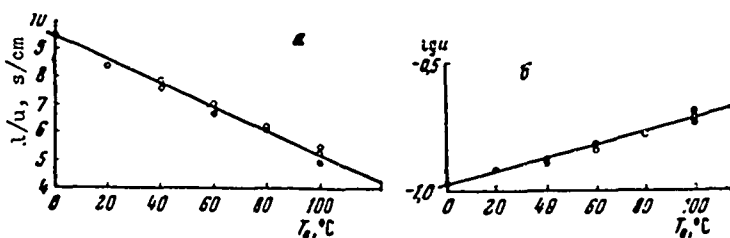


Fig. 9. Dependence of burning rate of gelatinized nitroglycerine (3% colloxylin is added) on initial temperature at atmospheric pressure [35]: a — in coordinates $1/u, T_0$; b — in coordinates $\lg u, T_0$.

With increase of interval, it is necessary to split it into several sections and to approximate real function $u(T_0)$ separately for every section (such procedure not infrequently leads to appearance of some kind "of bends" and "fractures," which in most cases hardly exist by experiment. Table 17 gives temperature coefficients for a number of volatile explosives.

From a comparison of tables 17 and 9, it is clear that for volatile VV, temperature coefficient $\beta_u \approx \beta_m$ is approximately 2-3 times higher than β_m for air gas mixtures. This will agree well with ideas expounded in division A of this paragraph about the fact that for volatile VV (containing NO_2 groups), burning takes place in at least two stages, where only the first of them (lcw-temperature) essentially affects burning rate.

Table 17. Value of Temperature Coefficient for Linear Burning Rate $\beta = d \ln u / dT_0$ for a Series of Volatile Explosives

Substance	p , [atm (abs.)]	β , deg ⁻¹	Temperature, °C
Nitroglycol	1	4,7 [34]	20-183
Nitroglycol gelated (3% collodion)	1	4,8 [35]	20-95
Nitroglycerine gelated (3% collodion)	1	6,5 [35]	10-95
Methyl nitrate	1	5,7 [35]	0-100
Dicel/coldinitrate	1	7,1 [35]	0-52,8
Trotyl	1	6,0 [35]	10-95
Hexogene	1	3,75 [47]	20-70
Tetryl	1	3,2 [47]	20-70
	20	4,3 [47]	20-70
		3,5 [47]	20-70

As was already noted in division A of this paragraph, in works [45, 47] it was proposed to use temperature coefficient for appraisal of effective temperature in the zone which determines burning rate. Formula (7) $\beta_u = E/2RT_r^2 = E/2RT_{\text{eff}}^2$ is used, whence

$$T_{\text{eff}} = \sqrt{\frac{E}{2R\beta_u}}. \quad (15)$$

Thus, here the problem solved is the reverse of the one which was solved in division E § 1. There (on the assumption that temperature in the zone determining burning rate is equal to thermodynamic temperature), function $u(T_r)$ was used for calculation of activation energy. Function $u(T_r)$ (where $T_r = f(T_0)$) cannot be used for calculation of activation energy for volatile VV, since it is not clear how T_{eff} changes (determining burning rate) with change of T_0 . Therefore in work [47] in a formula analogous to (7), activation energy was assumed and $T_r = T_{\text{eff}} = f(\beta)$ was calculated.

During the study of burning of condensed systems, the usual assumption is that activation energy for reactions taking place in zone of burning $T \geq 1000-1500^\circ\text{C}$ are the same as during slow thermal decomposition (at $T \approx 100-300^\circ\text{C}$).

Certainly, this assumption is not at all well founded. However, from § 1 it is clear that in the case of burning of gases, attempts to determine activation energy for reactions in zone of burning gave such a wide interval of values E that selection of this or that concrete value is a quite arbitrary operation. Therefore, both for gas and for condensed systems, the value of activation energy in equations of type (9), (10) and (7) should be considered a certain empirical constant. The most probable value of E for burning of gas mixtures is 30-40 kcal/mole. For volatile VV, data on slow thermal decomposition give for activation energy values within limits of 30-60 kcal/mole, but usually within 35-45 kcal/mole (Table 18).

Table 18. Value of Activation Energy from Data on Thermal Decomposition for Certain Volatile Explosives [35]

Substance	E, kcal/mole	Temperature °C	Substance	E, kcal/mole	Temperature °C
Methyl nitrate	30,5	212—239	Tetryl	53,5	220—270
Nitroglycol	39	85—105	Hexogene	47,5	213—299
Nitroglycerine	40,3	75—105	Hexogene in solution	41,0	—
	42,6	90—125		60,0	129,9—138,6
	45,0	125—150	Tetryl liquid	38,4	211—260
	50,0	150—190	Tetryl solid	52,0	—
PETN	47,0	160—225		36,6	—
PETN in solution	39,5	171—238			

It is also very essential that during appraisal of T_{eff} from (15), an error in activation energy has comparatively little effect on value T_{eff} , since activation energy is under the radical. From division A of the given paragraph, it is clear that for nitroglycol and tetryl T_{eff} calculated from (15) at $E = 37$ kcal/mole will agree well with the temperature of the first flame measured by thermocouple (see § 2A).

If for mass burning rate there is used not formula (13), but a more complete expression (type (10)), then instead of (7) we will obtain:

$$\beta = \frac{E}{2RT_r^2} + \frac{n+2}{2T_r}, \quad (7')$$

where n is order of reaction. Accordingly at a given β , T_{eff} will be higher than by formula (7):

$$T_{\text{eff}}(7') \simeq T_{\text{eff}}(7) + \frac{n+2}{43}.$$

However such a more precise definition of T_{eff} does not have special meaning, since the idea of effective temperature itself is approximate. In the end, formula (15) can simply be considered determination of effective temperature. In this case the question of its more precise definition, in general, becomes superfluous.

D. Dependence of Burning Rate on Density

The burning rate (u , mm/s) of solid explosives can depend on relative density of sample $\delta = \rho/\rho_{\text{max}}$, where ρ is real, g/cm^3 , ρ_{max} is the highest possible density of a given sample. The form of curve $u(\delta)$ depends on conditions of flow of reaction and presence of thermal losses. Let us enumerate certain special cases:

1. If reaction takes place in the gas phase and thermal losses are absent, mass burning rate $u\delta = \text{const} \neq f(\delta)$.

2. In the same conditions, but in the presence of thermal losses, $u\delta$ decreases with decrease of δ .

3. If reaction takes place in the condensed phase, where value δ does not change in wave of heating before zone of reaction, then in the absence of thermal losses, $u\delta \sim 1/\sqrt{\lambda\delta^n}$, where λ is the coefficient of thermal conduction in cal/cm·deg and n is order of reaction. In particular, at $n = 1$ and $\lambda \sim \delta$, will obtain $u\delta \sim \delta$.

4. Presence of thermal losses (under conditions of point 3) increases fall of $u\delta$ in proportion to decrease of δ .

5. If reaction takes place in melt at $\delta = 1$, then there take place the conditions shown in points 1 and 2.

Everything said in points 1-5 is valid in the absence of penetration of melt or heated gas into pores of fresh substance, i.e., in the absence of convection heat transfer from the zone of burning to fresh substance. Conversely, if such penetration occurs (usually in the region of small δ), the product $u\delta$ can be increased with decrease of δ .

Thus, function $u(\delta)$ is of noticeable theoretical interest, but its interpretation is sufficiently complex. Experimentally function $u(\delta)$ was studied mainly in connection with questions of breakdown of laminar burning (during penetration of products of burning into pores of charge). Regarding, however, function $u(\delta)$ in interval δ , where burning is laminar, this question was allotted considerably less attention.

Table 19 gives data on mass burning rate as a function of relative density for three volatile VV — tetryl, hexogene and PETN. For tetryl and PETN, mass rate remains practically constant during change of δ (within limits of scattering of results).^{*} For hexogene, it is possible to note very slight rise in m with increase of δ . At the beginning of this division, we already noted that this effect is sufficiently general. It is connected with the fact that heat emission in a unit of volume increases in proportion to δ , and thermal losses almost do not depend on δ .

Let us also give data for octogene taken from work [200] (Table 20).

^{*}For PETN mass burning rate (laminar) does not depend also on dimension of particles of initial powder from which charge is pressed. Such a result is completely natural. We will see below, however, that during burning of pure NH_4ClO_4 , burning rate can essentially depend on dimension of particles of initial powder.

Table 19. Dependence of Mass Burning Rate of Volatile Explosives on Relative Density of Charge

Explosive	Initial dimension of V particles, microns	P, atm	m(δ)								Lit. rature
Tetryl		1	δ	0,49	0,51	0,58	0,62	0,64	—	—	[35]
			$m, g/cm^2 \cdot s$	0,060 0,065	0,065	0,062	0,066	0,064	—	—	
Hexonite		1	δ	0,38	0,46	0,47	0,50	0,58	0,635	0,645	[48]
			$m, g/cm^2 \cdot s$	0,040	0,045	0,045	0,047	0,047	0,048	0,048	
Penta	~5	52	δ	0,50	0,51	0,66	0,73	0,88	—	—	[200]
			$m, g/cm^2 \cdot s$	0,99	0,85	0,86	0,88	0,99	—	—	
	100—400	52	δ	0,60	0,82	0,86	0,91	—	—	—	
			$m, g/cm^2 \cdot s$	0,99	1,00	0,87	0,99	—	—	—	

Table 20. Value of Mass Burning Rate of Octogene for Two Values of δ at Different Pressures

Pressure, atm	$m, g/cm^2 \cdot s$		Pressure, atm	$m, g/cm^2 \cdot s$	
	$\delta = 0,51$	$\delta = 0,87$		$\delta = 0,51$	$\delta = 0,87$
12,6	0,48	0,49	151	3,31	3,91
27,2	0,88	—	205	5,13	5,20
52	1,43	1,48			

§ 3. Laminar Diffusion Flame During Burning of Gas or Combustible Liquid

Diffusion flames of gas (or atomized solid or liquid fuel) are widely used in industrial furnaces. Study of diffusion flames is also interesting in the development of methods of fighting fires in oil tanks, etc. Although in technology in most cases it is necessary to deal with turbulent diffusion flames, a considerable part of scientific research pertains to laminar diffusion flames, which are more accessible for theoretical analysis and laboratory investigations. For condensed mixtures, where dimensions of particles of components are small, only laminar diffusion flames are of interest.

A. Diffusion Burning of a Stream of Combustible Gas

During the emanating of a stream of combustible gas into a tangled flow of air (or in fixed air) on the borders of the stream, burning starts.* Oxygen diffuses to flame through the whole thickened layer of products of burning. When flame approaches axis of stream of gas, burning is finished. A simple expression for height h of diffusion torch can already be obtained from considerations of dimension:

$$h(cm) \sim \frac{v \text{ (cm/s)} \cdot R^2(cm^2)}{D(cm^2/s)}, \quad (16)$$

where v is speed of gas; R is radius of stream of gas; D is coefficient of diffusion of oxidizer (in products of burning). By simple approximate computations (see [49]) it is simple to obtain a more complete formula for height of flame:

$$h = \frac{k\rho_r}{4C_\infty} \cdot \frac{rR^2}{D}, \quad (17)$$

where k is the number of grams of oxidizer necessary for oxidation of 1 g of fuel; ρ_r is the density of combustible gas, g/cm^3 ; C_∞ is concentration of oxidizer far off from torch, in g/cm^3 . According to (17), height of flame decreases with increase of C_∞ , for example, during transition from air to oxygen.** Obviously, with the help of formulas, analogous to (16) and (17), there can be found the height of flame in the case where stream of oxidizer emanates into combustible gas. Experimental data show that width of zone of reaction in diffusion flames is considerably larger than in homogeneous flames, and according to estimate [12], it can at 1 [atm(abs.)] be up to 1 cm for oxygen mixtures, and for air it can be several millimeters. Accordingly there decreases speed of liberation of heat in unit of volume of zone of reaction (for diffusion flame $CH_4 - O_2$, expenditure of oxygen is $\sim 6 \cdot 10^{-5}$ mole/ $cm^3 \cdot s$ and $\phi_{\max} \sim 10^1$ cal/ $cm^3 \cdot s$, whereas in homogeneous $CH_4 - O_2$ mixture, it is 4 mole/ $cm^3 \cdot s$ and $\sim 4 \cdot 10^5$ cal/ $cm^3 \cdot s$, respectively).

*It is important to note that diffusion flame cannot arbitrarily closely approach edges of burner due to presence of heat withdrawal in burner. Meanwhile mutual diffusion of oxidizer and fuel starts directly on cut of burner. Consequently, near burner edges, burning takes place in homogeneous mixture, and above it becomes diffusion burning. Although the region of homogeneous burning is small, it is very significant for diffusion torch stability [12].

**In works on diffusion flames, burning rate, as a rule, is not calculated, although it could have been defined as expenditure of gas through annular element of conical surface of flame, divided on area of this element. The fact is that defined by this method the burning rate would not be of constant mixture, but would depend on coefficient of diffusion of oxidizer (in products of reaction) and diameter of burner.

Let us now consider how approximate formulas (16) and (17) correspond to the experiment. From these formulas it follows that other things being equal, height of flame is proportional to volumetric flow rate vR^2 , cm^3/s (or mass flow rate $\rho_T vR^2$ $\text{g}/\text{cm}^2.\text{s}$) of combustible gas. Accordingly h/vR^2 does not have to depend on vR^2 . In work [23] there are given data of Burke and Schumann for a diffusion flame of methane in air (Table 21).

Table 21. Dependence of Height of Diffusion Flame of Methane in Air on Volumetric Flow Rate ($\pi R^2 v$) of Methane [23]

Expenditure of methane, l/h	h, cm	$h \pi R^2 v$	Expenditure of methane, l/h	h, cm	$h \pi R^2 v$
64,6	25,1	0,389	28,3	11,3	0,40
58,4	22,9	0,392	21,2	8,6	0,405
46,4	18,4	0,396	10,7	3,1	0,29
37,1	14,8	0,40			

From Table 21 it follows that with decrease of volumetric flow rate three times, value h/vR^2 remains practically constant and only at sufficiently small vR^2 , will it possibly essentially decrease.

From data of Vool, Gasli and Kapp given in work [50] for diffusion flame of city gas in air, it follows that length of flame h during constant volumetric flow rate (which in various series of experiments was from 1 to 100 cm^3/s) does not depend on diameter of burner in the 4-10 mm range. This will agree with (16) and (17).

From (16) and (17) it follows that $h \sim 1/D$. For flames of H_2 in air and CO in air, $h_{\text{CO}}/h_{\text{H}_2} \approx 2.5$, when $1/D_{\text{CO} \rightarrow \text{CO}_2} / 1/D_{\text{H}_2 \rightarrow \text{CO}_2} = 0.55/0.137 = 4$ (coefficients of diffusion are taken according to the data of Hirschfelder; $T = 273^\circ\text{K}$).

According to (16) and (17), h does not depend on pressure at constant volumetric flow rate, re-counted on normal conditions (i.e., 1 [atm(abs.)] and 273°K). This can be especially clearly seen from (17), where at $\rho_T vR^2 = \text{const} \neq f(p)$; $C_\infty \sim p$; $D \sim 1/p$ and $h \neq f(p)$, respectively. This conclusion has been confirmed experimentally by Burke and Schumann (for a CH_4 flame), in a very narrow interval of pressures (1-1.5 atm), however.

B. Burning Out of Combustible Liquid from Free Surface

Let us examine diffusion burning of liquid poured into a cylindrical vessel. If level of liquid with respect to edges of tube and temperature of tube walls are maintained constant, burning is stationary. At not too large a tube diameter, (according to estimate [49], at $d \leq 10$ mm for burning in air at 1 [atm(abs.)]), burning is laminar. These conditions will be examined by us.

Height h and form of flame during diffusion burning of liquid and gas obey the same laws. In particular, if speed of burning out of liquid is equal to w , there should be fulfilled $h/w(d/2)^2 = \text{const}$. Actually, for gasoline, kerosene, diesel fuel, solar oil, and ethyl alcohol, according to works [49, 51], $h/w(d/2)^2$ does not change much (nor monotonously) during change of d . In particular, for solar oil there are obtained the following values:

$d, \mu\text{m}$	3,7	5,0	6,0	7,1	11	20
$w, \text{mm/s}$	0,155	0,085	0,068	0,055	0,040	0,018
h, cm	3,0	4,0	4,4	4,9	7,9	11,8
$h/w(d/2)^2 \cdot 10^{-3} \text{s/cm}^2$.	5,7	7,5	7,2	7,1	6,5	6,4

However, during diffusion burning of gas, speed of stream of gas is arbitrarily assigned by the experimenter. Conversely, for liquid, speed of burning out establishes itself and depends both on thermodynamic parameters of liquid and on conditions of diffusion.

This speed w essentially differs from normal burning rate in homogeneous systems. On the one hand, it pertains only to pure fuel. Meanwhile, for every gram of fuel there is expended another 1.5-3.5 g of oxygen (depending upon nature of fuel). Therefore, mass burning rate of pure fuel $\rho_{\text{ж}} w$ (where $\rho_{\text{ж}}$ is density of liquid fuel) turns out to be approximately 2.5-5 times understated as compared to mass burning rate of corresponding stoichiometrical mixture of fuel with oxygen.

However, on the other hand, we relate $\rho_{\text{ж}} w$ not to surface of front of burning, but to cross section of tube. Data given in work [51] on height of flame show that at the expense of this factor, burning rate is overstated approximately 10-30 times (and the total turns out to be oversized 2-10 times). However, such comparison with burning rate of homogeneous systems is only of formal interest, inasmuch as we will see below that speed of burning out of liquid only very slightly depends on general height of torch.

We will now see what parameters affect speed of burning out of liquid (w).

1. With increase of diameter of burner, speed of laminar burn-up of liquid quickly drops (Fig. 10). During further increase of d (when burning has already ceased to be laminar), speed of burn-up ceases to drop, and then somewhat increases, apparently, tending toward a certain limit; however, this part of curve $w(d)$ will not be examined by us.

Maximum experimental value of burning rate (measured in the narrowest tubes) is [51] $0.022 \text{ g/cm}^2 \cdot \text{s}$ for gasoline and $0.016 \text{ g/cm}^2 \cdot \text{s}$ for kerosene (at 1 [atm(abs.)]).

2. With increase of concentration of oxygen in the environment, speed of burning out of liquid increases (Fig. 11): during transition from air (21% O_2 by volume) to a 50% $\text{O}_2 + 50\% \text{N}_2$ mixture, the speed of burning out of gasoline increases approximately 2.1 times, and the speed of burn-up of diesel fuel increases 3.3 times.

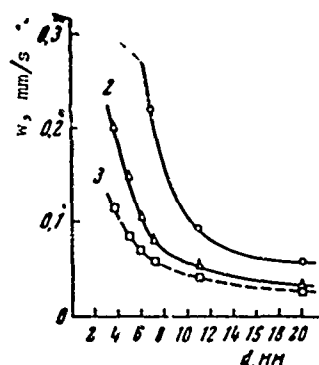


Fig. 10

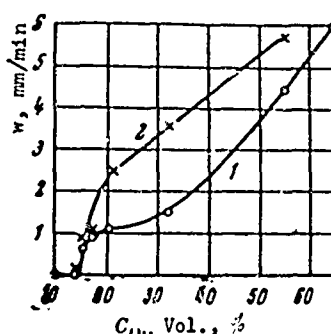


Fig. 11

Fig. 10. Dependence of speed of burning out of liquids on diameter of test tube [51]: 1 — auto-motive gasoline; 2 — tractor kerosene; 3 — diesel fuel.

Fig. 11. Dependence of speed of burning out of liquid on concentration of oxygen at $p = 1$ [atm(abs.)] [49]: 1 — diesel fuel; 2 — gasoline.

3. Speed of burn-up of liquids increases rapidly with increase of pressure [552]. Thus, for n-octane in a quartz crucible 11.3 mm in diameter* in the manometric bomb, there are obtained ($\rho_{\text{ж}}$ is density of liquid) the following values:

p_{O_2} , atm . . .	15	20	30	40	50	60
$\rho_{\text{ж}} w$, g/cm ² .s .	0.0052	0.0074	0.0120	0.0170	0.0230	0.0260

From comparison of these data with data of Tables 4 and 13, it is clear that $\rho_{\text{ж}} w$ for n-octane at high pressures is one or two orders lower than the burning rate of homogeneous air mixtures (not to mention oxygen) and one and a half to two orders lower than the burning rate of volatile VV. Dependence of mass burning rate of n-decane, benzene, gas oil and diesel fuel on pressure can be described by empirical formula $\rho_{\text{ж}} w \sim p_{O_2}^n$, where p_{O_2} is pressure of oxygen, but exponent $n = 0.96-1.07$ ($p_{O_2} = 10-40$ atm). For n-octane, exponent n decreases in proportion to increase of diameter of crucible (from $n = 1.2$ at $d_{\text{жБ}} = 11.3$ mm to $n = 0.83$ at $d_{\text{жБ}} = 22.6$ mm in the interval $p_{O_2} = 15-60$ atm). In work [52] the presence of strong dependence $\rho_{\text{ж}} w$ on p is connected with convection transfer of oxygen to flame. However, with increase of $d_{\text{жБ}}$, index n did not increase, but decreased. It remains unclear whether burning was laminar at high pressures.

*Equivalent diameter, calculated by value of free surface S of liquid
 $d_{\text{жБ}} = \sqrt{4S/\pi}$.

With increase of distance Δ between surface of liquid and edge of burner (during experiment $\Delta = \text{const} \neq f(t)$), speed of burn-up decreases;

Δ, mm	$w, \text{mm/s}$		Δ, mm	$w, \text{mm/s}$	
	ethyl alcohol	kerosene		ethyl alcohol	kerosene
0	0,060	0,055	4,5	0,028	0,022
0,5	0,052	0,047	6,5	0,017	0,0067
2,5	0,042	0,040			

At sufficiently large Δ , burning fades.

5. Speed of burn-up depends on nature of liquid. Thus, for example, in work [51] there is obtained:

Combustible liquid	$w, \text{mm/s}$		Combustible liquid	$w, \text{mm/s}$	
	$d = 6 \text{ mm}$	$d = 20 \text{ mm}$		$d = 6 \text{ mm}$	$d = 20 \text{ mm}$
Automatic gasoline . . .	0,300	0,057	Diesel fuel	0,070	0,028
Tractor kerosene	0,1065	0,032	Solar fuel	0,068	0,018

Value w for the fastest burning and the slowest burning liquid ($w_{\text{max}}/w_{\text{min}}$) is 3-4.5, i.e., approximately as much as the analogous relationship for air mixtures or volatile VV at 1 [atm(abs.)]. Work [49] gives w approximately for 30 different liquids in quartz burners of large diameter (62 and 106 mm). In particular, at $d = 62 \text{ mm}$ there are obtained the following values of w (in mm/s):

Propane	0,052	Automotive gasoline . .	0,028
Ethyl ether	0,048	Carbon bisulfide	0,028
Toluene	0,045	Acetone	0,023
Turpentine	0,040	Methyl alcohol	0,020
Aviation gasoline . . .	0,035	Kerosene	0,017
Xylene	0,033	Solar oil	0,013

In this case $w_{\text{max}}/w_{\text{min}} = 4$. The influence of the nature of the liquid on w somewhat decreases with increase of burner diameter.

6. Speed of liquid burn-up according to [49], decreases with increase of thermal conduction of burner material and the thickness of its walls. Thus, for example, for ethyl alcohol there is obtained:

burner	w, mm/s	
	d = 8 mm	d = 10 mm
Glass	0,077	0,057
Steel . . .	0,072	—
Copper . . .	—	0,045

Let us consider now the question of what factors determine speed of liquid burn-up from a free surface. It is possible to consider that w is basically influenced by the sections of flame closest to the liquid surface. Therefore, the connection between speed of burn-up w and height of flame h is practically one-sided: height of flame is proportional to w (see above), but speed of burning out only slightly depends on the full height of the flame.

The quantity of substance reacting in that part of the flame which essentially affects burning rate (in the "zone of influence") is limited by speed of feed of oxidizer from surrounding volume (in particular, it increases with increase of concentration of oxidizer in volume). Quantity of heat emanated, moreover, in the limits of the zone of influence, of course, depends on the nature of the liquid; however, heat of burning calculated for a mole of oxygen ($Q_{\text{сгор}}$ kcal/mole O_2), for a majority of combustible liquids lies within very narrow limits:

Methyl alcohol	108	Ethyl ether	100
Glycerine	101,5	Xylene	99,5
Benzene	101	Acetone	98,2

Such a result is natural, since even heat of combustion of hydrogen and carbon (on a mole of O_2) do not differ very much (115.6 and 94 kcal/mole O_2), and the contribution of heat of formation of liquid is not very considerable.

However, flow of heat q from flame to surface of liquid can essentially depend on nature of liquid (in particular, radiant flow is great for smoking flames of benzene, xylene, etc., and is small for the transparent flames of the lowest alcohols and esters).

This flow is expended on preheating and evaporation of liquid:

$$q = \rho_{\text{ж}} w \frac{\pi d^2}{4} [c_{\text{ж}} (T_{\text{исп}} - T_0) + Q_{\text{исп}}] . \quad (18)$$

Hence

$$w = \frac{q}{\frac{\pi d^2}{4} \rho_{\text{ж}} [c_{\text{ж}} (T_{\text{исп}} - T_0) + Q_{\text{исп}}]} , \quad (18')$$

where $c_{\text{ж}}$ is heat capacity, cal/g·deg; $Q_{\text{исп}}$ is heat of evaporation of liquid, cal/g. Consequently, influence of nature of liquid on w is combined not only with changes of value q , but also with changes of thermophysical constants of the liquid.

The data given in Table 22 show (in agreement with the conclusions of work [49]) that there is correspondence between speed of burn-up and expenditures of heat

Table 22. Speed of Burning Out and Expenditure of Heat on Heating and Evaporation of a Unit of Volume for Combustible Liquids

Combustible liquid	w, mm/s	$\rho_{\text{ж}}[c_{\text{ж}}(T_{\text{исп}} - T_0) + Q_{\text{исп}}]$ ккал/см ³
Benzene	0,032	105
Ethyl ether	0,043	67,5
Xylene	0,033	116,5
Acetone	0,023	120
Methyl alcohol	0,020	230
Glycerine	0,0067	361

$\rho_{\text{ж}}[c_{\text{ж}}(T_{\text{исп}} - T_0) + Q_{\text{исп}}]$ on heating and evaporation of liquid (see the series benzene - xylene - glycerine and ethyl ether - acetone - methyl alcohol).

The influence of q on speed of burning out appears during transition from benzene to ethyl ether (see Table 22), when value $\rho_{\text{ж}}[c_{\text{ж}}(T_{\text{исп}} - T_0) + Q_{\text{исп}}]$ decreases approximately 1.6 times, but speed of burning out, nevertheless, drops (apparently, because of decrease of radiant flow).

We will make several remarks with respect to function w(p), w(d), etc.:

a) increase of w with increase of p can be connected not only with convection transfer, but also with the fact that flame in homogeneous mixture* (for edges of burner) approaches the liquid surface with increase of p.

b) decrease of w with increase in d is connected with the fact [49] that supply of heat from the flame at the expense of heat conduction take place only on the periphery of the burner and is proportional to burner diameter. Supply of heat by radiation is proportional to cross section of burner. Accordingly, $w \sim (ad + bd^2)/d^2 = a/d + b$, that is, w decreases with increase in d;

c) a certain part of the heat emanated in the flame is removed by the burner walls. Part of this heat goes to preheating of surface layers of liquid (and increases w). However, because of the low speed of burning out of liquid, a large part of the heat removed by the wall disperses (since the burner is not thermally insulated) - this decreases w.

*Formation of homogeneous mixture is connected with the fact that the flame is located at a certain distance from the burner edges this distance is limited by speed of heat withdrawal to burner walls, but mixing of fuel vapors with gaseous oxidizer starts immediately on cut of burner.

§ 4. Burning of Solid Particles and Liquid Drops

Burning of atomized solid and liquid fuel is an important component part of the working process in air and liquid jet engines, in diesel engines, and in industrial furnaces on coal dust or liquid fuel. It is necessary to note that during burning of gas, there is possible formation of particles of carbon in the flame (both in a diffusion flame and in homogeneous flame, especially with increase in pressure [12]). Burning is tightened, and height of torch increases.

The most important parameters for burning of atomized fuel are time of ignition $\tau_{\text{ВОСПЛ}}$ and burn-up time $\tau_{\text{ГОР}}$, since they determine the necessary dimensions of the combustion chamber.

In general, the burning rate of a particle depends both on speed of feed of oxidizer from surrounding volume, and on speed of reaction at front of burning. This can be recorded in very graphic form [26]. Let us assume that the concentration (in g/cm^3) of oxidizer is equal to C_∞ in the surrounding volume and C_ϕ on the front of burning. For stationary process on 1 cm^2 of front of burning in 1 s, there reacts as much oxidizer as is fed to it at the expense of diffusion from the surrounding volume. For the case of a reaction of the first order, it is possible to write:

$$k_{\text{КИН}} C_\phi = k_{\text{ДИФ}} (C_\infty - C_\phi), \quad (19)$$

where $k_{\text{КИН}}$ and $k_{\text{ДИФ}}$ are constants of speed of reaction and diffusion rate in cm/s . Hence we find concentration of oxidizer on front of burning $C_\phi = C_\infty k_{\text{ДИФ}} / (k_{\text{КИН}} + k_{\text{ДИФ}})$. Accordingly, speed of consumption of oxidizer in front of burning $m_{\text{ОК}}$ (in $\text{g/cm}^2 \cdot \text{s}$) (proceeding from which it is easy to calculate particle burning rate, (34) is equal to:

$$m_{\text{ОК}} = k_{\text{КИН}} C_\phi = \frac{C_\infty}{1/k_{\text{ДИФ}} + 1/k_{\text{КИН}}}. \quad (20)$$

If $k_{\text{ДИФ}} \gg k_{\text{КИН}}$ (i.e., diffusion does not limit speed of process), burning takes place in kinetic conditions; $C_\phi \approx C_\infty$; $m_{\text{ОК}} \approx k_{\text{КИН}} C_\infty$. Conversely, if $k_{\text{ДИФ}} \ll k_{\text{КИН}}$ (i.e., speed of reaction is very great), burning takes place in diffusion conditions; $C_\phi \approx 0$; $m_{\text{ОК}} \approx k_{\text{ДИФ}} C_\infty$.

Experimental data show (see below) that the burning of drops of liquid fuels and particles of metals usually obeys well enough the laws characteristic for diffusion conditions (see below).

A. Formula for Speed of Diffusion Burning of a Spherical Particle

Using the method proposed in work [30], we will examine the burning of a single particle of fuel in a quiescent gas. Diffusion of the i -th gas to particle will be described by equation:

$$D \frac{d}{dr} \left(r^2 \frac{dC_i}{dr} \right) - v r^2 \frac{dC_i}{dr} = 0, \quad (21)$$

where C_i is molar concentration, mole/cm³; D is coefficient of diffusion, cm²/s; v is speed of gas due to presence of Stefanovskiv flow in cm/s. As usual, it is accepted that density of gas and coefficient of diffusion do not depend on coordinates. We consider quasi-steady-state solution.

Let us record continuity equation ($\rho \neq f(r)$):

$$v r^2 = \text{const} = v_\phi r_\phi^2, \quad (22)$$

where r_ϕ is radius of front of burning, $v_\phi = v|_{r=r_\phi}$. Boundary conditions:

$$C_i|_{r \rightarrow \infty} = C_{i\infty}; C_i|_{r=r_\phi} = C_{i\phi}. \quad (23)$$

Integrating (21) taking into account (22) and (23), we will obtain:

$$\frac{dC_i}{dr} \Big|_{r_\phi} = \frac{r_\phi}{D} \frac{C_{i\infty} - C_{i\phi}}{r_\phi^{n-1}}. \quad (24)$$

Flow of i -th gas near front of burning is equal to:

$$q_{i\phi} = -D \frac{dC_i}{dr} \Big|_{r_\phi} \cdot v_\phi C_{i\phi} = v_\phi \left(C_{i\phi} \frac{r_{i\phi} - C_{i\phi}}{r_\phi^{n-1}} \right). \quad (25)$$

The value of $C_{i\infty}$ is known, since initial composition of gas is given. However, values $C_{i\phi}$ and v_ϕ cannot be assigned beforehand and have to be found from additional conditions. First of all, it is necessary to use the condition that on the front of burning, there does not occur accumulation of substance. In other words, the flow of every element (for example, O) in the composition of gases transferred to front of burning (for example, O₂), should be equal to the flow of this element in the composition of gases transferred from the front (for example, H₂O, CO₂). To illustrate the method, we will examine burning of hydrocarbon fuel in air on the assumption that the only products of combustion are CO₂ and H₂O. Then the condition named will be recorded in the form:*

$$(q_{O_2})_\phi + 0.5 (q_{H_2O})_\phi + (q_{CO_2})_\phi = 0, \quad (26)$$

*Such a formulation of the problem is approximate, since, besides CO₂ and H₂O flow from the front of burning to the surrounding volume, there exists a small flow of products of combustion (and nitrogen) to the surface of the drop

here flows q_i are expressed in mole/cm².s; accordingly, condition (26) means that the number of moles of oxygen transferred to the front of burning (in 1 s through 1 cm²), is equal to the number of moles of oxygen in the composition of products of burning, transferred from the front. Further, it is obvious that

$$(N_i)_\phi = 0. \quad (27)$$

If in a molecule of fuel, the ratio between the numbers of atoms of hydrogen and carbon is equal to n_H/n_C , then in the example examined:

$$\frac{2(q_{H_2O})_\phi}{(q_{CO_2})_\phi} = \frac{n_H}{n_C}. \quad (28)$$

Further, in diffusion conditions of burning, concentration of oxidizer (and concentration of fuel) on front of burning is minute. In the example examined:

$$(C_{O_2})_\phi \approx 0. \quad (29)$$

Finally, from the equation of state of an ideal gas:

$$\sum_i C_i \phi = p/RT. \quad (30)$$

It is convenient to go from measured concentration $C_i = (m_i/\mu_i)/V$ mole/cm³ to dimensionless volume concentration $\phi_i = V_i/V$. Putting C_i into the equation of state $pV_i = \frac{m_i}{m_i} RT = C_i VRT$, we will obtain $C_i = \phi_i \frac{p}{RT}$ and condition (30) will be recorded in the form:

$$\sum_i \phi_i \phi = 1. \quad (30')$$

In equations (26)-(29) it is sufficient simply to replace C_i with ϕ_i , since factor p/RT is reduced.

[FOOTNOTE CONTINUED FROM PRECEDING PAGE]

toward flow of products of fuel. In strict formulation of the problem, besides solution of equation of diffusion (21), in external (with respect to front of burning) region there should have been solved an analogous equation for the internal region (between front of burning and drop) and presence of jump of density and speed of gas on front should have been considered. However, due to numerous simplifications accepted from the very beginning of the solution ($\rho_T \neq f(r)$; $D \neq f(r)$; schematic composition of products of combustion, quasi-stationarity of solution), such complication of the problem is not justified.

System (26)-(29), (30') consists of five equations and contains five unknowns: $(\vartheta_{H_2O})_\phi, (\vartheta_{CO_2})_\phi, (\vartheta_{N_2})_\phi, (\vartheta_{O_2})_\phi, r_\phi$, which can be determined from this system. The expression for v_ϕ will be obtained in the form:

$$v_\phi = \frac{D}{r_\phi} \ln(1 + A), \quad (31)$$

where

$$A = \frac{[(\vartheta_{O_2})_\infty + 0.5(\vartheta_{H_2O})_\infty + (\vartheta_{CO_2})_\infty] - [0.5(\vartheta_{H_2O})_\phi + (\vartheta_{CO_2})_\phi]}{0.5(\vartheta_{H_2O})_\phi + (\vartheta_{CO_2})_\phi} = \frac{(\vartheta_{N_2})_\infty - (\vartheta_{N_2})_\phi}{(\vartheta_{N_2})_\phi}. \quad (32)$$

During burning of a single particle in air, it is possible approximately to take $(\vartheta_{H_2O})_\infty \simeq 0, (\vartheta_{CO_2})_\infty \simeq 0, (\vartheta_{O_2})_\infty = 0.21, (\vartheta_{N_2})_\infty \simeq 0.79$.

Let us now extract the equation connecting burning rate of particle with diffusion rate of oxidizer to front of burning. Let us assume that 1 mole of fuel reacts with k moles of oxidizer. Then

$$4\pi r_\phi^2 (q_{O_2})_\phi \mu_{top} dt = -k \cdot 4\pi r_K^2 dr_K \rho_{top}, \quad (33)$$

where μ_{top} is molecular weight of fuel; t is time; r_K is radius of drop (particle) of fuel; ρ_{top} is density of fuel (solid or liquid) in g/cm^3 .

Hence burning rate of particle:

$$w = \frac{dr_K}{dt} = - \left(\frac{r_\phi}{r_K} \right)^2 \frac{(q_{O_2})_\phi \mu_{top}}{k \rho_{top}}. \quad (34)$$

Putting $(q_{O_2})_\phi$ into (34), we obtain:

$$w = \frac{1}{r_K} \cdot \frac{r_\phi}{r_h} D \frac{p}{RT} \frac{(\vartheta_{O_2})_\infty \mu_{top}}{k \rho_{top}} \frac{\ln(1+A)}{A}, \quad (35)$$

where $D = D_0(p_0/p) (T/T_0)^n$ ($p_0 = 1$ [atm(abs.)], $T_0 = 273^\circ K$, $D_0 = D|_{p_0; T_0}$, $n = 1.75-2.0$).

Ratio r_ϕ/r_K will be found from the condition that in a steady-state operation,*

*During burning of particles steady state of two types is possible: 1) if thermal conduction of particle and time after beginning of burning are sufficiently great, temperature is identical at any point of the particle and does not depend on time; 2) if thermal conduction of the particle is very small (or if we study burning of liquid on a porous burner), at the surface of the particle, a stationary wave of heating is established.

the quantity of heat, fed to the particle is equal to expenditures of heat on evaporation of particle:

$$\lambda' \frac{dT}{dr} \Big|_{r_K} = \rho_{\text{rop}} w Q_{\text{исп}} = \rho' v_K' Q_{\text{исп}}, \quad (36)$$

where λ' , ρ' , v_K' is the coefficient of thermal conduction, density, and speed (at the surface of the drop) of fuel vapors. Temperature gradient $\frac{dT}{dr} \Big|_{r_K}$ will be found from heat-conduction equation $\frac{a'}{r^2} \frac{d}{dr} \left(r^2 \frac{dT}{dr} \right) - v' \frac{dT}{dr} = 0$ (in region $r_K \leq r \leq r_\phi$) at boundary conditions $T|_{r_K} = T_K = f(p)$ and $T|_{r_\phi} = T_\phi$. Hence

$$\frac{dT}{dr} \Big|_{r_K} = \frac{v_K'}{a'} \frac{T_\phi - T_K}{e^{\frac{v_K' r_K}{a'} \left(1 - \frac{r_K}{r_\phi} \right)} - 1}, \quad (37)$$

where $a' = \lambda'/\rho'c'$ is temperature transfer of fuel vapors. Putting (37) into (36), we will obtain:

$$w = \frac{\lambda'}{c' \rho_{\text{rop}}} \cdot \frac{1}{r_K \left(1 - \frac{r_K}{r_\phi} \right)} \cdot \ln \left[1 + \frac{c' (T_\phi - T_K)}{Q_{\text{исп}}} \right]. \quad (38)$$

We obtained a system of two equations (35) and (38) with two unknowns w and r_ϕ/r_K . Hence we will obtain:

$$w = - \frac{dr_K}{dt} = \frac{1}{r_K \rho_{\text{rop}}} (N + L), \quad (39)$$

$$\frac{r_\phi}{r_K} = 1 + \frac{L}{N}, \quad (40)$$

where there are introduced the symbols $L = \frac{\lambda'}{c'} \ln \left[1 + \frac{c' (T_\phi - T_K)}{Q_{\text{исп}}} \right]$ and

$N = D_0 T_K^{-1} \frac{P_0}{RT_0^2} \frac{1}{k} (\partial \alpha)_\infty \mu_{\text{rop}} \frac{\ln(1 + L)}{L}$. Let us note that value N does not depend on pressure and value L depends very slightly on pressure (with increase in pressure, T_K can increase, and $Q_{\text{исп}}$ can decrease). Integrating (39), we will obtain:

$$d^2 = d_0^2 - \kappa t, \quad (41)$$

$$\tau = d_0^2 / \kappa, \quad (42)$$

where d_0 is particle diameter at $t = 0$; $\kappa = 8(N + L)/\rho_{\text{rop}}$; τ is time of burning of particle (from $d = d_0$ to $d = 0$). Consequently, time of burning of particle is proportional to the square of its initial diameter and does not depend on pressure.

B. Experimental Data on Burning of Particles

During the study of burning of particles and drops, there are used at least three different methods:

1) drop or particle freely moves in flow of gas and the time of its burning is measured;

2) drop or particle is suspended on a thin thread (usually quartz) and its radius is measured as a function of time (and also full time of burning);

3) liquid fuel penetrates from within through porous ball and burns on its surface. There is measured expenditure of liquid, i.e., speed of its burning.

In the first and second methods, burning is nonstationary or quasi-stationary; in the third method, burning is stationary. The first method is used for drops measuring from ~100 microns to several millimeters (for solid fuels there were studied smaller particles — from 1 to 10 microns). The second and third methods are used for comparatively big particles ($d \geq 1$ mm).

We will stop at first on burning of drops of liquid fuels. First of all, let us note that a spherically symmetrical flame is observed only for very small drops. At $d \geq 1$ mm, the flame is greatly drawn out (Fig. 12) due to the presence of free convection (in works [55, 56] there were conducted experiments in a freely falling chamber. In this case the flame becomes spherically symmetrical, and burning rate decreased approximately 2 times due to the absence of convection).



Fig. 12. Burning of ethyl alcohol in air on porous sphere at a pressure of 650 mm Hg (a) and 240 mm Hg (b) [54].

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In spite of distortion of shape of flame, many (but, naturally, not all) experimental results will agree with the conclusions of the theory obtained for the spherically symmetrical case. First of all the theory agrees with dependence of speed and time of burning on diameter of drop. Thus, works [55, 57] show that at coordinates d^2 , t , experimental points (for seventeen liquids) lie well on straight lines, i.e., satisfy equation (41).

In works [54, 58] it is shown that experimental points well satisfy dependence

$$\dot{M} = 4\pi r_k^2 \frac{dr_k}{dt} \cdot \rho_{\text{top}} \sim r_k$$

(this dependence emanates from (39)).*

Work [58] also gives data on dependence of time of burning τ on diameter of drop d_0 . According to (42), it should be the case that $\tau \sim d_0^2$. Exactly such a result is obtained for drops of tetralin and paraffin ($d_0 = 150$ -600 microns). For drops of kerosene, the exponent is somewhat higher (~ 2.3).

Work [54] shows that burning rate of ethyl alcohol on a porous sphere 5.5 mm in diameter increases with increase of oxygen concentration (in mixtures with nitrogen or helium):

O ₂ , % by volume	}		25	40	63	100
Burning rate		O ₂ + N ₂ . .	0,0042	0,0057	0,0072	0,0085
g/s		O ₂ + He . .	0,0055	0,0074	0,0083	0,0095

However, increase of burning rate is less considerable than this follows from theory.

According to [58], burning rate of drops of furfuryl alcohol, tetralin, decane, and amylacetate increases with increase of pressure (in mean $\sim p^{0.25}$). This result also will not agree with the above-stated theory and, possibly, is combined with influence of convection.

At 1 [atm(abs.)] experimental value κ in (41) and (42) during burning of organic liquids in air lies within limits of $(0.7-1.0) \times 10^{-2}$ cm²/s. It is possible to show that at 1 [atm(abs.)], mass burning rate of drops (calculated per unit of surface of front of burning, taking into account mass of oxidizer) becomes comparable with mass burning rate of homogeneous combustible gas - air mixtures (see Table 1) only for very small drops ($r_k \lesssim 10$ microns). Decreasing drop size, it is possible to obtain formally very high calculated speeds of burning; however, sufficiently shallow drops will succeed completely in evaporating to ignition.

Burning of particles of metals is most frequently studied under conditions in which particle moves freely in flow of air (or oxygen), and also in products of burning of gas (or condensed) system (see Figs. 13, 14, 15). In the last case, burning of metal occurs at the expense of reduction of H₂O (to hydrogen) or CO₂ (to CO), etc. As compared to experimental data on liquid fuel, data on burning of metal particles are few in literature; they are less complete, and divergence between works of different authors is considerable. Therefore, experimental data can be compared with conclusions of diffusion theory within very limited limits. We saw that during burning of drops of liquid fuels, dependence of speed and time of burning on diameter of drop agreed well with theoretical dependence (in particular,

* $\dot{M}$ is burning rate of drop in g/s.

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Fig. 13

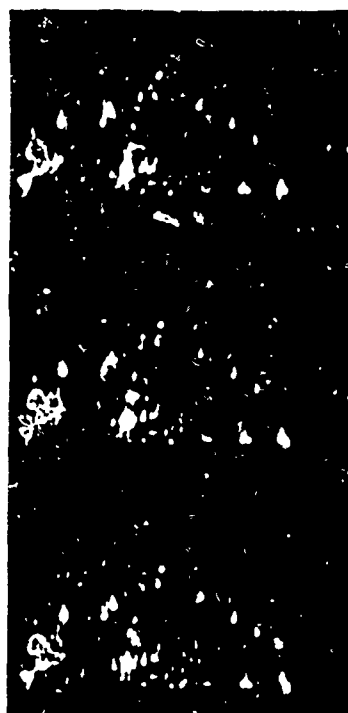


Fig. 14



Fig. 15

Fig. 13. Tracks of aluminum particles (30-35 microns), burning at $p = 1$ [atm(abs.)] in flow of gas [228]. At end of track, one may see splitting of particles. Temperature and composition of gas: a - $T = 2390^\circ\text{K}$; 34% O_2 ; 0.6% H_2O ; b - $T = 2410^\circ\text{K}$; 32% O_2 ; 17% H_2O .

Fig. 14. Frames (speed of filming 3800 frames/s) of burning of particles of aluminum above surface of powder ($p = 14$ atm) [76].

Fig. 15. "Explosion" of burning particles of titanium [61]. Dimension of particles 150-420 microns; burning in oxygen; ignition by gas flame.

time of burning $\tau \sim d_0^2$). For particles of metals, dependence $\tau(d)$ is studied in narrow intervals d and on the basis of a small number of points. For aluminum there is obtained in work [59] $\tau \sim d_0^{1.5}$, and in work [60] $\tau \sim d_0^{1.8}$ (on two points $d_0 \approx 60$ microns and $d_0 \approx 95$ microns). Work [61] gives $\tau \sim d_0^{2.56}$ for magnesium and $\tau \sim d_0^{1.59}$.

Work [60] notes that time of burning rapidly decreases with increase of oxygen concentration. For aluminum particles ($d_0 = 53$ -66 microns) in an atmosphere of products of combustion of $\text{CO} - \text{O}_2 - \text{N}_2$ ($\sim 2500^\circ\text{K}$, 1 [atm(abs.)]) there is obtained:

O_2 , % by volume . . .	23,3	30	40	50	60
$\tau \cdot 10^3$, s	12,7	8,4	6,5	5,4	4,5

The strong influence of concentration of oxidizer will agree with theory. Conversely, the decrease noted in that same work [60] of time of burning of particles of aluminum with increase of pressure (Table 23) will not agree with

Table 23. Dependence of Time of Burning of Particles of Aluminum on Pressure. Experiments Were Conducted in Combustion Products of NH_4ClO_4 - Paraformaldehyde Mixture [60]

Mixture ratio, % by weight			d_{Al}, μ	Time, s					
NH_4ClO_4	PHA	Al		21 atm	22 atm	23 atm	24 atm	25 atm	26 atm
85	15	0,01	89-103	—	11,5	9,7	7,9	7,3	7,3
90	10	0,1	53-66	9,6	7,4	5,9	4,8	4,7	4,7
95	15	0,01	53-66	5,5	4,2	3,6	3,5	3,5	3,5
76	24	0,01	53-66	5,5	4,2	3,6	3,5	3,5	3,5

diffusion theory and requires additional considerations for its explanation (it is possible that with increase of pressure there somewhat increases combustion efficiency and combustion temperature of the NH_4ClO_4 - paraformaldehyde mixture, in the combustion products of which the experiments were conducted. Furthermore, with increase of pressure, there increases particle density of aluminum in a unit of volume of flow and, accordingly, radiation thermal losses decrease).

In Table 24 there are collected certain data available in literature on burning of particles of aluminum and magnesium in different gas mixtures at atmospheric pressure. For comparison there is also given time (calculated on (42)) of burning of benzene drops in air (experimental data on burning of liquid drops 10-50 microns in diameter were not at our disposal).

The data of works [59, 60, 62] for aluminum are similar among themselves, and in work [63], time of burning of aluminum is considerably longer. A complicating circumstance here is the formation of hollow Al_2O_3 shells (Fig. 16) (burning is tightened). Up to now there is insufficient clarity in the question of the conditions under which these shells will be formed and the conditions under which they will not be formed; whether they exist around every particle or only around a certain fraction of the particles; whether they exist during the whole time of burning of a particle, etc. Another complicating circumstance is the division of particles during burning - fragmentation of particles, "explosion" of particles, etc. (see Fig. 13 for an aluminum particle and Fig. 15 for a titanium particle). This phenomenon, apparently, is connected with the accumulation of vapors of metal under oxide film and its subsequent sudden break. It is natural that in the presence of division of particles, time of burning can essentially decrease.

Magnesium particles (at $d = 50$ microns) burn considerably faster than aluminum particles. Let us note that during transition from air to $2 \text{ O}_2 + 8 \text{ He}$ mixture (percent by volume of oxygen remains constant) time of burning essentially decreases (approximately 1.5 times). This will qualitatively agree with theoretical considerations, inasmuch as coefficient of diffusion of oxygen in helium is $0.638 \text{ cm}^2/\text{s}$, and in air is $0.178 \text{ cm}^2/\text{s}$ [64].

Table 24. Certain Source Material on Time of Burning of Magnesium and Aluminum Particles in Different Gas Mixtures at Atmospheric Pressure

Fuel	Composition of gas in surrounding volume	$\tau \cdot 10^4, s$							Literature
		$d = 10 \mu$	$d = 20 \mu$	$d = 30 \mu$	$d = 40 \mu$	$d = 50 \mu$	$d = 80 \mu$	$d = 120 \mu$	
Al	Products of burning of $C_2H_4-O_2-N_2$ (in products 5.4% O_2 ; 18.4% H_2O)				10.5 ($d_0 = 35 \mu$)	19			[62]
	Products of burning of $CO-O_2-N_2$ (in products 7.9% O_2 ; 0.5% H_2O)				6.6 ($d_0 = 35 \mu$)	12			[62]
	Products of burning of $C_2H_4-O_2-N_2$ (in products 5.5% O_2 ; $T = 2510^\circ K$)		4 ($d_0 = 23 \mu$)			13			[59]
	Combustion products of CH_4-O_2	2-9	7-19	16-33	28-49	44-64			[63]
Mg	Air					1.85	6.2	16.8	[64]
	$2O_2 : 8Ar$					1.75	5.85	15.8	[64]
	$2O_2 : 8He$					1.3	4.3	11.5	[64]
C_2H_4	Air	0.078	0.31	0.7	1.24	1.94	5	11.2	

Time of burning (and consequently, burning rate) of magnesium particles is on the same order as for organic fuels. Inasmuch as r_{ϕ}/r_K for magnesium is



Fig. 16. Spheres of Al_2O_3 ($d \approx 150$ microns), which form during the burning of aluminum particles ($d = 70$ microns) [229]. Part of spheres is crushed to show that they are hollow.

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considerably less than for organic fuels due to essentially higher heat of evaporation (1260 cal/g for magnesium against ~100 cal/g for a majority of hydrocarbon

fuels), burning rate of magnesium per unit of surface of front of burning will be higher than for organic fuels.

Till now we have examined the case of reactions occurring in one zone at one or another distance from the particle surface. However, during burning of ammonium perchlorate balls in an atmosphere of combustible gas (see [231, 232]), there are two zones of reaction. Near the surface of the ball there is located a kinetic flame of products of decomposition of NH_4ClO_4 (see § 10, 19), and further away there is a diffusion flame. Regularities of such burning are complex (see § 10), and, of course, do not have to correspond to simple diffusion theory. Nonetheless, for burning of NH_4ClO_4 in C_3H_8 and NH_3 ratio (4:1) $d^2 = d_0^2 - \kappa t$ turned out to be valid. However, this result still does not testify to the diffusion character of burning. First of all, the form of function $d(t)$ during the burning of an NH_4ClO_4 ball in inert atmosphere* is unclear. Furthermore, in this case for value κ , there are revealed dependences not peculiar to diffusion conditions of burning. Thus, during addition of 1% copper chromite, value κ was increased approximately 1.5 times. With increase of pressure (from 1 to 5 atm), value κ essentially increased ($\kappa \sim p^{0.57}$). The influence of kinetic factors appeared also in the fact that KClO_4 , NH_4NO_3 and KNO_3 balls, in contrast to NH_4ClO_4 balls, could not stably burn in an atmosphere of propane (at $p \leq 3$ atm). Further, for NH_4ClO_4 it turned out that κ increases with increase of d_0 , although, according to theory, $\kappa \neq f(d_0)$.

Constant κ weakly (and linearly besides) increased with increase of speed of gas ($\kappa = \kappa_0 + \kappa_1 v$). At 1 [atm(abs.)], value κ_0 in C_3H_8 was $\sim 0.036 \text{ cm}^2/\text{s}$; in NH_3 it was near $0.027 \text{ cm}^2/\text{s}$. For comparison there is given value κ_0 during the burning of drops of kerosene-in oxygen ($0.01\text{--}0.015 \text{ cm}^2/\text{s}$) and hydrazine in oxygen ($0.035 \text{ cm}^2/\text{s}$).

To a large extent diffusion theory does not correspond with results of experiments on burning of NH_4ClO_4 balls in $\text{H}_2 - \text{N}_2$ mixture. In this case $d^3 = d_0^3 - kt$ is obtained, where k almost did not depend on hydrogen concentration.

C. Flame Propagation Velocity in Suspensions of Atomized Fuel in Air and Oxygen

During burning of atomized fuel, a basic parameter is burning rate (or time of burning) of an individual particle. However, for certain problems, interest is also aroused by flame propagation velocity by flow of suspension of fuel particles in gaseous oxidizer (see [77-79] and others).

*By analogy with burning of gas mixtures, increase of burning rate with decrease of d is probable. It is not excluded that we will obtain

$$d^2 = d_0^2 - \kappa t.$$

O. I. Leypunskiy [65] noted that burning of suspensions can be considered burning of homogeneous mixture, taking into account the fact that reaction in zone of burning obeys laws characteristic for burning of particles. Subsequently we will stop on this question in greater detail, and here we will expound on certain experimental results [77-78]. There were studied suspensions of aluminum powder in air (at $\alpha = 3.15-1.26$) and of graphite powder in oxygen at $\alpha = 0.52-0.46$. In all cases burning rate in the region investigated α increased with increase of percentage of fuel (Table 25).

Table 25. Linear and Mass Flame Propagation Velocity in Suspensions of Aluminum in Air [77]. (Bunsen Burner 19 mm in diameter)

$C_{Al}, \text{mg/l}$	α	$u, \text{cm/s}$		$m, \text{g/cm}^2 \cdot \text{s}$	
		$d < 10 \mu$	$d < 30 \mu$	$d < 10 \mu$	$d < 30 \mu$
100	3,15	21	15	0,0275	0,0196
150	2,1	28,5	19	0,0387	0,0254
200	1,58	34,5	23	0,0486	0,0324
250	1,26	39,5	26	0,0577	0,038

At $\alpha = 1.26$ the mass burning rate of an aluminum - air suspension is on the same order as the mass burning rate of stoichiometrical air mixtures of saturated hydrocarbons. Speed of flame in graphite suspensions is essentially less than in aluminum suspensions.

Consideration of experimental data is hampered by the fact that speed of flame greatly depends on methodical parameters (type of burner and its diameter).

§ 5. Burning at the Expense of Reaction in Condensed Phase

During burning of condensed substances, it is possible to imagine conditions under which a significant part of the heat (and in the maximum case of so-called "flameless burning," all the heat) is emanated in the course of reaction in solid or liquid phases. Such conditions, from a theoretical point of view, should sharply differ from burning of homogeneous gas and volatile systems, since in condensed phase the diffusion rate of products of burning (and, in particular, active particles) into fresh substance is practically equal to zero, and propagation of burning can take place only at the expense of transmission of heat by thermal conduction.

Furthermore, it is natural to assume that absolute value of burning rate and its dependence on pressure, initial temperature, density, etc., for such conditions of burning will also essentially differ from analogous dependences for gas systems.

At first glance it would have been possible to expect that for conditions when all heat is emanated in condensed phase, absolute value of burning rate will be very high (since density of condensed phase is high and, furthermore, its thermal conduction also exceeds thermal conduction of gas near front of burning for volatile systems). It was possible to expect also that speed "of flameless"

burning would not depend on pressure (and, in particular, should stably flow in deep vacuum). Mass speed "of flameless" burning should strongly drop with decrease of density of system (since speed of reaction decreases with fall of concentration of fresh substance). Finally, for those substances for which "flameless" burning constitutes conditions with incomplete isolation of heat of reaction (and therefore low-temperature rate), a high temperature coefficient should be observed.

In literature there is not described a single substance for which all the enumerated regularities would be observed. However, quite a few substances are described, for which there clearly appears part of such regularities (the remaining enumerated regularities are absent or are not investigated).

1. In literature there is described a comparatively large group of quick-burning explosives (VV). Data for some of them are given in Table 26.

Table 26. Linear and Mass Burning Rate of Certain Quick-Burning Explosives at 1 [atm(abs.)]

Substance	u, cm/s	m, g/cm ² ·s	Literature
Lead styphnate $C_4H(NO_2)_4O \cdot Pb \cdot H_2O$	26—27	100	[66]
70% lead styphnate + 30% trinitro- triazidobenzene $C_4(NO_2)_3(N_3)_2$	26	—	[67]
40% lead styphnate + 60% talc	14,5	—	[31]
Diazodinitrophenol $C_6H_3(NO_2)_2ON_2$. .	2,15	3,12	[31]
Mercury fulminate $Hg(ONC)_2$	1,55	5,9	[31]
Potassium picrate $C_6H_2(NO_2)_3OK$. .	1,50	2,74	[31]
Tricycloacetone peroxide $C_3O_6(CH_3)_6$	0,95	1,16	[31]

From comparison of Tables 26, 1 and 13, it follows that at 1 [atm(abs.)] mass burning rate of quick-burning VV by an order (and for styphnate lead — by 2.5 orders) exceeds burning rate of oxygen mixtures and volatile VV.

For styphnate lead, besides very high absolute velocity of burning, there is observed a second criterion — the burning rate of lead styphnate almost does not depend on pressure. At a pressure in bomb of 15 mm Hg* u ≈ 25-26 cm/s, and at 50 atm, burning rate is increased to 33-35 cm/s and remains without changes in the interval, 50-400 atm [66].

*It is necessary to note that (as follows from laws of conservation of mass and impulse) pressure on front of burning for quick-burning substances can noticeably exceed pressure (p_∞) in surrounding volume (this effect becomes essential at low p_∞). The calculation made in work [68], shows that in the case of lead styphnate, pressure on front of burning cannot decrease lower than several atmospheres.

For quick-burning lead and potassium picrates there is also a considerable interval of pressure where speed of their burning practically does not depend on pressure. Thus, for lead picrate the burning rate at 100 [atm(gage)] is ~26 cm/s, and at 300 [atm(gage)], it is 31 cm/s [66]. For potassium picrate according to work [69], burning rate is practically constant at 10-80 atm and is ~6 cm/s. In work [70] for potassium picrate, there is obtained a more complex dependence: burning rate is maximal ($u_{\max} \approx 6$ cm/s) at 5-6 [atm(abs.)] atmosphere, then slowly decreases to 4.3 cm/s with increase of pressure to 25 [atm(abs.)], and then remains constant in the interval, 25-125 [atm(abs.)].

However, below a certain pressure, the burning rate of lead and potassium picrates starts to drop quickly and finally burning ceases (for potassium picrate at 500 mm Hg, but for lead picrate even at 20 atm).

For mercury fulminate in the whole studied range of pressure (10 mm Hg to 150 atm), burning rate increases with increase of pressure (at $p \leq 1$ [atm(abs.)] u (cm/s) = $0.4 + 1.1 p$ ([atm(abs.)]), and at $p > 1$ [atm(abs.)] $u \sim p^{0.5}$). In work [31] it is shown that at $p \leq 1$ [atm(abs.)] burning rate increases with increase of pressure also for trinitrotriazidobenzene and tricycloacetone peroxide. For mercury fulminate there was studied [31] dependence of mass burning rate on relative density $\delta = \rho/\rho_{\max}$. Mass burning rate starts to increase immediately with decrease of density — at first insignificantly, and then very fast.

Temperature coefficient $\beta_u = d \ln u / dT_0$ for mercury fulminate is equal to $5.1 \cdot 10^{-3} \text{ deg}^{-1}$ (in the interval 20-105°C [31]), i.e., has the same value as for liquid nitroethers (see Table 17).

2. Conditions of flameless burning for ballistite powders were revealed and investigated in detail by P. F. Pokhil [41, 71]. Such conditions can be observed only in vacuum (in comparatively narrow interval of pressures) and at raised initial temperature. Burning is flameless not only in a conditional sense, (i.e., in the sense that all heat of reaction is emanated in condensed phase), but also in a literal sense, i.e., in this case, above surface of powder, no glow is observed even in complete darkness. Speed of flameless burning does not depend on pressure (with sufficient increase of pressure above surface of powder there appears flame, but burning rate starts to increase with pressure (Table 27).

Table 27. Dependence of Burning Rate of Pyroxylin Powder on Pressure in Atmosphere of Nitrogen [71]
 $T_0 \approx 90^\circ \text{C}$

$P, \text{ mm Hg}$	$u, \text{ mm/s}$	$P, \text{ mm Hg}$	$u, \text{ mm/s}$	$P, \text{ mm Hg}$	$u, \text{ mm/s}$	$P, \text{ mm Hg}$	$u, \text{ mm/s}$
1	0,8	18	0,8	120	1,1	550	2,4
2	0,8	30	0,8	200	1,4	650	2,7
5	0,8	70	1,0	280	1,6	720	2,8
9	0,8			410	2,0		

Temperature coefficient of burning rate $\beta_u = d \ln u / dT_0$ for these conditions of burning is great and is $11.2 \cdot 10^{-3} \text{ deg}^{-1}$ (in the interval $90-140^\circ\text{C}$ [71]).

Independence of burning rate from pressure for conditions of flameless burning was also observed for nitroglycerine powder (in the interval of $2-40 \text{ mm Hg}$; $u = \text{const} = 0.5 \text{ mm/s}$).

It is necessary to note that absolute value of speed of flameless burning (for a given range of pressure) should be considered high. At least, at 20 mm Hg , mass burning rate of pyroxylin and nitroglycerine powders is 1-1.5 orders higher than mass burning rate of gaseous mixtures on the basis of oxides of nitrogen.*

Mass burning rate (m , $\text{g/cm}^2 \cdot \text{s}$) at 20 mm Hg of pyroxylin and nitroglycerine powders ($T_0 \approx 100^\circ\text{C}$) [71] and gaseous mixtures ($\alpha = 1$) on the basis of oxides of nitrogen ($T_0 \approx 20^\circ\text{C}$) [9] is given below:

Powder		System	
pyroxylin	... 0.128	$\text{C}_2\text{H}_2 - \text{N}_2\text{O}$	... 0.0071
nitroglycerine	... 0.080	$\text{H}_2 - \text{N}_2\text{O}$	... 0.007
		$\text{C}_2\text{H}_2 - \text{NO}_2$	... 0.0154
		$\text{H}_2 - \text{NO}_2$	... 0.0047
		$\text{C}_2\text{H}_4 - \text{N}_2\text{O}$	... 0.0043

Accordingly, at 2 mm Hg , this difference can be increased by approximately one more order.

Conversely, speed of "usual" burning of powder has the same order as speed (mass) of burning of gaseous mixtures on the basis of oxides of nitrogen. Thus, according to work [72], at 1 [atm(abs.)] and 18°C , the burning rate of nitroglycerine powder is $0.08 \text{ g/cm}^2 \cdot \text{s}$; for mixtures based on NO (see Table 2), mass burning rate (for different fuels) lies within limits of $0.02-0.106 \text{ g/cm}^2 \cdot \text{s}$; for mixtures based on NO_2 it lies within limits of $0.035-0.226 \text{ g/cm}^2 \cdot \text{s}$, etc.

3. For nitroglycerine powder at atmospheric pressure, in work [72] there was observed fast increase of temperature coefficient of burning rate with increase of initial temperature. The value of temperature coefficient of burning rate $\beta_u = d \ln u / dT_0$ for nitroglycerine powder (caloricity 870 cal/g) at atmospheric pressure is the following:

Temperature, $^\circ\text{C}$	$\beta \cdot 10^3, \text{deg}^{-1}$	Temperature, $^\circ\text{C}$	$\beta \cdot 10^3, \text{deg}^{-1}$
-180 ± -100	2.5	$0-20$	7
-100 ± -40	2.2	$20-40$	10.3
-40 ± 0	2.16	$40-80$	14
$-10 \pm +10$	4.6	$80-100$	15.4
		$100-120$	16.1

*It is true that data for gaseous mixtures pertain to room temperature, but increase of initial temperature to $\sim 100^\circ\text{C}$, naturally, does not change the order of magnitude of the burning rate, since for gas mixtures $\beta_m = d \ln m / dT_0 \sim 10^{-3}$.

In work [161] for powder H at 1 [atm(abs.)], there was also observed an analogous effect, but value β was somewhat lower (at $T_0 = -78-+40^\circ\text{C}$ $\beta \approx 6 \cdot 10^{-3} \text{ deg}^{-1}$; at $T_0 = 40-130^\circ\text{C}$ $\beta \approx 12 \cdot 10^{-3} \text{ deg}^{-1}$).

Increase of β with increase of T_0 (for powder H) was also observed at high pressures (10, 20 and 50 atm; [73]).

The most natural explanation for this effect consists in the fact that with increase in T_0 , there increases the role of reactions in the low-temperature zone, in particular, in the condensed phase.*

As for absolute value of burning rate, (in the studied interval T_0) it is still close to the burning rate of volatile explosives.

4. Mass burning rate of pyroxylin noticeably decreases with decrease of density (Table 28).

Table 28. Dependence of Mass Burning Rate (m , $\text{g/cm}^2 \cdot \text{s}$) of Pyroxylin on Density [74]
Tube 10 mm in diameter; room temperature, in nitrogen

Density, g/cm^3	m , $\text{g/cm}^2 \cdot \text{s}$			Density, g/cm^3	m , $\text{g/cm}^2 \cdot \text{s}$		
	$p = 21 \text{ atm}$	$p = 25 \text{ atm}$	$p = 31 \text{ atm}$		$p = 21 \text{ atm}$	$p = 25 \text{ atm}$	$p = 31 \text{ atm}$
0.8	1.21	—	—	1.3	1.35	1.66	1.78
1.0	1.29	1.44	1.58	1.5	1.63	1.77	1.98

Lowering of burning rate (with decrease of ρ) for pyroxylin is much more strongly expressed than for volatile VV (where it is combined with decrease of heat emission in unit of volume and corresponding increase of role of thermal losses, see § 2G).

Thus, experimental data show that in certain conditions, it is possible to observe very distinctly certain criteria, apparently, characteristic for burning at the expense of reaction in condensed phase.** At the same time it is clear that usually there is a number of complicating circumstances combined with the fact that in most cases, reaction in condensed phase takes place only partially.

*It is paradoxical, however, that for pyroxylin powder studied in work [235], temperature coefficient not only did not increase, but even essentially decreased with increase of T_0 (at $T_0 < 60^\circ\text{C}$ $\beta \approx 19 \cdot 10^{-3} \text{ deg}^{-1}$, and at $T_0 > 60^\circ\text{C}$ $\beta \approx 6 \cdot 10^{-3} \text{ deg}^{-1}$).

**For powders an obligatory condition of the appearance of such criteria is sufficiently high initial temperature of powder.

First of all it is necessary to consider here the phenomenon of dispersion. It was discovered for the first time during the burning of mercury fulminate in a vacuum [75]. On the walls of the bell, where burning was conducted, there appeared an intense deposit of extraordinarily finely divided mercury fulminate contaminated with mercury. If a deposit is collected from the walls and pressed, then such "burning" mercury fulminate burns the same as fresh mercury fulminate.

The late phenomenon of dispersion was investigated in detail by P. F. Pokhil during burning of ballistite powders [41, 71]. During burning in vacuum, there was dispersed up to 70% of the initial powder.

In a number of theoretical works, an attempt has been made to obtain an expression for burning rate especially at the expense of a reaction in the condensed phase in the presence of dispersion (in principle, burning rate can depend on pressure). Two different formulations of the problem are examined.

1. It is assumed that burning rate is determined by speed of liberation of heat within the limits of sections of condensed phase still not detaching from charge (it is assumed that reaction in dispersed particles and, all the more so, reaction in flame in no way affect, burning rate). Average density of substance in zone of reaction is close to density of initial charge. Temperature in zone of reaction is low and is equal to T_{Π} (temperature on surface of charge). With such an approach, burning rate drops with increase of degree of dispersion* η_{Π} .

Unfortunately, the laws of dispersion have been weakly studied by experiment. Therefore, theoretical expressions (see, for example, [202]), in which functions $u(p)$, $u(T_0)$, etc. are expressed through functions $\eta_{\Pi}(p)$, $\eta_{\Pi}(T_0)$, etc.; cannot be compared even qualitatively with experiment.

In work [215] there is examined the special case where η_{Π} is determined by solubility of gaseous half-finished products in liquid layer on surface of powder. Concrete estimates and comparison with experiment are not given.

2. In work [238] it is accepted that burning rate is determined by speed of liberation of heat in dispersed particles or liquid films, forming layer of foam. Average density of reacting layer is close to density of gas, but temperature can considerably exceed T_{Π} . If velocities of particles and gas are equal, function $u(p)$ is close to $u \sim \sqrt{p}$.

Examined monophasic models of burning still poorly correlate with experiment. It is clear, however, that for the most interesting systems, burning is knowingly multistage and cannot be described with the help of similar models.**

*In theoretical work [202], a conclusion was reached especially high burning rate in the absence of dispersion (for pyroxylin powder it is estimated at $u \approx 2500 \text{ mm/s} \neq f(p)$). This conclusion up to now has no experimental confirmations (experimental value of u for pyroxylin powder at 1 [atm(abs.)] and 90°C is $\sim 3 \text{ mm/s}$ [71]).

**In particular, for ballistite powders experimental dependence $u(p)$ is strengthened at sufficiently high pressures [239], when theoretical function $u(p)$, combined with decrease of degree of dispersion, should, conversely, be saturated at high pressures.

During the burning of ballistite powders, there are three zones of heat emission. According to P. F. Pokhil, one should distinguish reaction layer of condensed phase, smokegas zone, and zone of flame (see [41, 71, 204, 205] and others). In American literature (see [240-244] and others) the terms foam-, fizz-, flame-zone are accepted.

Experimentally the laws of multistage burning were investigated both by analysis of experimental data on functions $u(p)$, $u(T_0)$, etc., and by measurement of profile of temperatures and composition of gas, measurement of distance between zones, etc. (see [41, 71, 102, 103, 106, 109, 130, 131, 169, 204-206, 242-248] and others).

In particular, for ballistite powders at low pressures, a basic role is played by reaction in the condensed phase [41, 71, 240]. At a pressure of several tens of atmospheres, burning rate, apparently, is determined by reaction in smokegas zone* [45, 240], and flame renders only insignificant influence on burning rate [240, 242, 247]. Conversely, at a sufficiently high pressure, in the opinion of the authors of works [240, 242], the zone of flame becomes leading.

In a number of theoretical works an attempt is made to modify the solution of Zel'dovich and Frank-Kamenetskiy (or analogous solutions) by series transition from one stage to another taking into account heat emission at a given stage and flow of heat from other stages (there was examined the more particular problem where there is one zone of reaction and assigned flow of heat from without) (see [203, 207-212, 240, 241] and others). However, it was not possible up to now to find an expression which would give in evident form the dependence of speed of multistage burning on pressure, initial temperature, etc., at assigned kinetics of reaction to every stage.

Only the case where one of the stages is leading (see § 10A) is sufficiently clear from a theoretical point of view. However, experimental methods which would permit establishing the presence of one leading stage of burning have not been worked out up to now.

Conversely, the case where one of the zones practically does not affect burning rate yields well to experimental investigation since it is located too distantly from the surface of charge and other zones of burning (at least in a given zone and the main part of heat of reaction was emanated) (see, for example, [247]). Attention of theoreticians was attracted by the given case from the point of view of how a similar zone is maintained at a constant distance from surface of charge and does not contact flow. The most convincing explanation (see [213, 214, 240, 246]) is that in such zone there occurs self-ignition of half-finished products formed on preceding stages (this ensures automatic fine adjustment under burning rate).

CHAPTER II

BASIC PROCESSES DETERMINING RATES OF COMBUSTION OF CONDENSED MIXTURES. ELEMENTS OF THEORY OF BURNING OF CONDENSED MIXTURES

Burning of mixtures of solid fuels and oxidizers is more complex than the other forms of burning examined above. In general, it is multidimensional and multistage and depends on both kinetic and diffusion factors. Burning rate of condensed mixtures depends only on those processes which occur in a sufficiently narrow zone adjoining the fresh mixture. Only in the maximum case of sufficiently finely dispersed mixtures of volatile components does burning take place in purely kinetic conditions and front of burning become flat.

§ 6. Speed of Mixing of Fuel and Oxidizer

So that components of condensed mixture can interact, with sufficient speed their mixing should take place in zone of heating or zone of reaction.

A. Influence of Aggregate State on Character and Mixing Rate of Components

Great influence on speed and character of mixing of components is rendered by the aggregate state of fuel and oxidizer in zone of heating and zone of reaction. If the fresh substance is a mixture of two solid components, then in zone of heating and zone of reaction, every component can either remain in solid phase or be melted or gasified. Six variants are possible [81]:

1) $TB + TB$; 2) $TB + Ж$; 3) $TB + Г$; 4) $Ж + Ж$; 5) $Ж + Г$; 6) $Г + Г$.

Mixing of components before the beginning of a reaction can occur only under the condition that fuel and oxidizer (or products of their destruction) possess sufficient mutual solubility. This condition is always satisfied in the sixth case and is almost surely not satisfied in the third and fifth cases, since the number of grams of gas which can be dissolved or sorbed by a gram of liquid or solid is minute as compared to usual weight ratios between components in condensed mixtures.

Thus, in cases 6) $Г + Г$, and also in cases 1) $TB + TB$; 2) $TB + Ж$ and 4)

Ж + Ж (during condition of sufficient solubility of components), mixing can partially (and for sufficiently thinly dispersed mixtures — completely) take place before the beginning of reaction. Conversely, in cases 3) TB + Г and 5) Ж + Г, which correspond to burning of suspension of nonvolatile particles or drops in flow of gas, mixing can take place only simultaneously with reaction [81]. Aggregate state of components can strongly affect speed of mixing and width of zone of mixing. In cases 6) Г + Г, and also 1) TB + TB; 2) TB + Ж; 4) Ж + Ж zone width of mixing, according to (17), is proportional to

$$h_{\text{new}} \sim kmD^2/C_{\infty}D_0$$

where m is mass burning rate. The aggregate unit state affects value $C_{\infty}D_0$, where C_{∞} is concentration of diffusing component (far from surface of contact of components); D is coefficient of diffusion. At too large a diameter of particles of components, mixing takes place at the expense of molecular diffusion. At sufficiently great diameters of particles, convection mixing can also become essential (see below).

B. Value of Coefficient of Molecular Diffusion in Different Media

There is a large number of data on coefficient of diffusion (especially for gases). However, all data for gases pertain either to self-diffusion, or to diffusion in binary mixtures (or in air). For multicomponent mixtures (to which there belong products of combustion of any real systems), there are neither experimental data nor well-founded methods of calculation of coefficient of diffusion. The majority of experimental data for binary mixtures pertains to low temperatures.*

Usually for coefficient of diffusion in gases, there is used formula:

$$D = D_0 \frac{p_0}{p} \left(\frac{T}{T_0} \right)^n, \quad (43)$$

where D_0 is coefficient of diffusion at $p_0 = 1$ [atm(abs.)] and $T_0 = 273^\circ\text{K}$, cm^2/s . Depending upon nature of mixture, value D_0 can change at least one order. High values of D_0 emanate mixtures with hydrogen. For saturated hydrocarbons D_0 monotonously decreases with increase of length of chain of hydrocarbon [30, 82, 83]:

gas (in mixture with air)	H_2	CO_2	CH_4	C_2H_6	C_3H_{12}	$\text{C}_{10}\text{H}_{22}$
D_0 cm^2/s [30] ..	0,611	0,138 [82]	0,196	0,108	0,067	0,046

*In work [88] there are data on coefficient of diffusion of vapors of certain metals in flame at $T \approx 1400\text{-}1800^\circ\text{C}$.

Formula (43) is empirical; value of index n is determined for a given mixture by experimental points. Therefore formula (43) does not allow reliable extrapolation beyond the limits of the investigated interval of temperatures. For sufficiently wide intervals of temperatures it is customary to take $n = \text{const}$, where n lies within limits from 1.5 to 2.0 (see [84, 30] and others). Value $n = 1.75$ is frequently taken. However, during more exact approximation of experimental data, n is considered to depend on temperature. Thus, in work [85] for coefficient of self-diffusion of CO_2 in the interval 200-1700°K, it is accepted that

$$D(\text{cm}^2/\text{s}) = 0.0967 (T/273)^n, \text{ where } n = 1.81 + 0.035 (T/273).$$

Function $D \sim 1/p$, which follows from (43), is somewhat weaker than the real function [82, 86, 87]. Thus for system $\text{H}_2 - \text{N}_2$ in work [86], the following values are obtained:

$p, \text{ atm}$	$pD, \text{ atm} \cdot \text{cm}^2/\text{s}$		$p, \text{ atm}$	$pD, \text{ atm} \cdot \text{cm}^2/\text{s}$	
	$T = 273^\circ \text{ K}$	$T = 473^\circ \text{ K}$		$T = 273^\circ \text{ K}$	$T = 473^\circ \text{ K}$
1	0.708	1.86	100	0.570	1.425
50	0.570	1.44	200	0.562	1.474

In most cases value D is given without indicating the concentration to which it pertains. Meanwhile function $D(C)$ [36, 87] is noticeable. Thus, for example, for $\text{N}_2 - \text{CO}_2$ mixture at 301°K, there is obtained [87]:

Mixture	$D, \text{ cm}^2/\text{s}$	
	$p = 6 \text{ atm}$	$p = 21 \text{ atm}$
$\sim 0 \text{ N}_2 + \sim 1.0 \text{ CO}_2$	0.027	0.005
$0.5 \text{ N}_2 + 0.5 \text{ CO}_2$	0.030	0.0065
$0.75 \text{ N}_2 + 0.25 \text{ CO}_2$	0.032	0.007

In this case D increases with increase of content of lighter component, which seems natural.

For coefficient of diffusion in liquid and solid phases, there is used formula.

$$D = D_0 e^{-E/RT}, \quad (44)$$

where D_0 has meaning of coefficient of diffusion at $T \rightarrow \infty$, and E is activation energy. Values D_0 and E are determined by experimental points and depend on nature of substance much more than values D_0 and n in formula (43) for gas mixtures.

Coefficient of diffusion in liquid and solid phases depends on concentration of diffusing substance. In aqueous solutions, dependence $D(C)$ is weak and ambiguous enough: depending upon nature of substance, coefficient of diffusion can decrease, remain approximately constant, or increase [82] with increase in concentration. There are also data [82] on dependence $D(C)$ during diffusion in alloys. During diffusion of aluminum and zinc in copper, the value of coefficient of diffusion quickly increases with increase in concentration:

C , at. % . . .	$C_{Al} = 4$	$C_{Al} = 12$	$C_{Zn} = 4$	$C_{Zn} = 12$
D , cm^2/s (800°C)	$4.21 \cdot 10^{-10}$	$2.61 \cdot 10^{-9}$	$3.72 \cdot 10^{-10}$	$3.33 \cdot 10^{-9}$

Dependence of coefficient of diffusion in solid and liquid phases on pressure is apparently weak. Thus, in work [82] for coefficient of self-diffusion in liquid CO_2 there is given:

p , atm	71	138	397
D , cm^2/s . . .	$4.56 \cdot 10^{-5}$	$4.01 \cdot 10^{-5}$	$3.2 \cdot 10^{-5}$

We saw (see (17)), that speed of mixing depends on product $C_\infty D \sim \rho D$ (for gas $C_\infty D \sim \rho D \sim (D_0 p_0 n / RT_0) (T/T_0)^{n-1} f(p)$). Let us estimate value $C_\infty D$ for diffusion in gas, liquid, and solid phases.

For binary gas mixtures, value D_0 lies within limits $\sim 0.05-1 \text{ cm}^2/\text{s}$. Taking $n = 1.75$, we will obtain at 1000°C a sufficiently reliable appraisal $D_{1 \text{ atm}} \approx 0.7-1.5 \text{ cm}^2/\text{s}$ and $\rho D = 3 \cdot 10^{-4} - 3 \cdot 10^{-3} \text{ g/cm} \cdot \text{s}$. At 2000°C it is possible to give only a rough estimate (distant extrapolation). At $n = 1.75$, we will obtain $D_{1 \text{ atm}} = 2-40 \text{ cm}^2/\text{s}$; $\rho D \approx 5 \cdot 10^{-4} - 5 \cdot 10^{-3} \text{ g/cm} \cdot \text{s}$.

Appraisal of values $C_\infty D$ for diffusion in liquid and solid phases is much wider (and less reliable). Certain data on coefficient of diffusion are given in Table 29.

There are also data [82] on diffusion in solid and melted salts at $T \leq 400-700^\circ\text{C}$.

During diffusion through oxide films, value C_∞ is limited by solubility of metal or oxygen in oxide. For solid Cr_2O_3 at 1000°C $C_{\text{Cr}} \leq 10^{19} \text{ atoms/cm}^3 \approx 10^{-3} \text{ g/cm}^3$ [93]. Inasmuch as, however, in most cases data on C_∞ are absent, we will estimate product $C_\infty D$ from above, taking $C_\infty \approx 1 \text{ g/cm}^3$ (Table 30).

Thus, at $T \leq 100^\circ\text{C}$, speed of mixing in the gas phase is considerably higher than in the liquid phase and all the more so in the solid phase. With increase

Table 29. Interval of Values $D(\text{cm}^2/\text{s})$ for Diffusion in Liquid and Solid Phases

System	Temperature, °C	
	1000	2000
Fe → FeS (liquid), Fe → Cu ₂ S (liquid) [89] Si; Ti; V; Nb in liquid cast iron [90] Fe; Co; Ca; Si; Nb; V; Ti; Zr in melt 45% CaO, 47% Al ₂ O ₃ , 6% MgO, 2% B ₂ O ₃ [91] Fe; Ni; Ca; Si; Nb; V; O in melt 40% CaO; 40% SiO ₂ ; 20% Al ₂ O ₃ [91, 92]	$6 \cdot 10^{-13} - 3 \cdot 10^{-4}$ (in most cases $10^{-8} - 10^{-3}$)	$5 \cdot 10^{-5} - 5 \cdot 10^{-2}$
Cr → Cr ₂ O ₃ (TB.) [93] O → UO ₂ (TB.) [94], Al ₂ O ₃ (TB.) [95] O → Ti; Zr; Nb; Ta (TB.) [96]	$5 \cdot 10^{-12} - 4 \cdot 10^{-7}$ (in most cases $10^{-8} - 10^{-7}$)	$10^{-9} - 10^{-4}$ (in most cases $10^{-3} - 10^{-4}$)

of temperature, this difference decreases, but at 2000°C, speed of mixing in gas is still several orders higher than in the solid phase (especially considering that C_∞ in the solid phase can be small). However, speed of molecular transfer in melt at 2000°C already becomes of one order with speed of transfer in gas.

Table 30. Limits of Change $C_\infty D$ (g/cm·s)

T, °C	Gas	Liquid	Solid phase
1000	$3 \cdot 10^{-4} - 3 \cdot 10^{-3}$	$6 \cdot 10^{-12} - 3 \cdot 10^{-4}$	$5 \cdot 10^{-22} - 4 \cdot 10^{-7}$
2000	$5 \cdot 10^{-4} - 5 \cdot 10^{-3}$	$5 \cdot 10^{-3} - 5 \cdot 10^{-2}$	$10^{-9} - 10^{-4}$

It is necessary to consider that besides molecular diffusion in the gas phase there can take place convection mixing of components (see section G of this paragraph). Speed of convection transfer in liquid melt should be much lower than in gas because of essentially higher viscosity of melt. However, for systems the components of which are melted before gasification (or are gasified with formation of liquid residue), there can take place spraying of liquid layer by gas and transfer of drops of liquid (or dissolved) component to zone of reaction.

C. Speed of Gasification of Fuels and Oxidizers

Inasmuch as aggregate state of components strongly affects speed of their mixing, the question of speed of gasification of components is of interest.

During burning of usual disordered mixtures, where crystals of oxidizer are alternated with layers of fuel all the time, heating and gasification of

every particle take place in nonstationary conditions. Speed of gasification $w = w(t)$ of crystal of oxidizer and layers of fuel can be measured with the help of high-speed filming. However, for several reasons this is a difficult matter (filming must be conducted with sufficient increase with very short exposure; filming is greatly hampered by presence of flame and smoke, and in a number of cases also by the presence of condensed residue on burning surface, etc.). It is not surprising, therefore, that even the best series of photographs of burning surface permit arriving at only very limited conclusions.

Speed of nonstationary gasification should greatly depend on expenditures of heat on heating and gasification of particle. If in direct proximity of surface of particle there is located kinetic flame of products of its decomposition, then, with respect to zone of burning on the whole, heat of gasification of particles should be calculated, taking into account liberation of heat in given flame. From this point of view, gasification of NH_4ClO_4 and NH_4NO_3 is an exothermic process [97, 118] (although gasification of surface of NH_4ClO_4 and NH_4NO_3 crystals goes on with absorption of heat: $\text{NH}_4\text{ClO}_4(\text{cr}) \rightarrow \text{NH}_3(\text{g}) + \text{HClO}_4(\text{g}) - 58$ kcal/mole; $\text{NH}_4\text{NO}_3(\text{cr}) \rightarrow \text{NH}_3(\text{g}) + \text{HNO}_3(\text{g}) - 40.5$ kcal/mole). Conversely, gasification of fuels requires considerable heat addition from zone of burning (heat of depolymerization of typical polymers is 10-25 kcal/mole (Table 31), and heat of evaporation of corresponding monomers is 5-10 kcal/mole [119]).

Table 31. Heat of Polymerization and Products of Destruction of Certain Polymers

Polymer	Heat of polymerization kcal/mole	Products of destruction
Polymethyl methacrylate	13 [99] 10-13 [249]	Monomer (95% [128]; >90% [249])
Polyisobutyl	12.3-12.8 [99] 10 [249]	Monomer 20-50% [128, 249] dimer, trimer, and tetramer [249]
Polystyrene	16.1-16.7 [99] 17 [249]	Monomer 30-65% [99]; ~65% [249] dimer, trimer, and tetramer [249]
Polybutadiene [249]	17-20	Monomer 20-30%; major fragments
Polyethylene	22-25 [249]	Monomer (up to 1% [99, 128, 249]); major fragments [249]

Comparative data on speed of nonstationary gasification of various substances, apparently, could have been obtained by determining time of gasification of particle of assigned dimension, which at time $t = 0$ is suddenly placed into flow of gas at assigned pressure and temperature. The shorter the time of gasification τ , the higher the speed of gasification $\bar{w} = d/2\tau$. However, such appraisal was not conducted experimentally.

Due to difficulties connected with determination of nonstationary speed of gasification, for appraisal of relative ability of different substances to gasify, there are used data obtained during slow thermal decomposition, and also during stationary gasification of sufficiently thick plate of fuel or oxidizer (at the expense of heat addition from heated plate or flow of hot gas, or during burning of plate of fuel in oxidizing atmosphere, or during burning of plate of oxidizer in combustible gas — and in the case of NH_4ClO_4 and NH_4NO_3 also in inert atmosphere). Certainly, one should consider that laws of gasification can strongly differ during transition from one of these cases to another and all the more so can differ from the laws of nonstationary gasification under conditions of burning.

In particular, it is necessary to stop on influence of pressure. In spite of scantiness of experimental data, it is possible to consider that pressure does not influence (or very weakly influences) speed of gasification during slow thermal decomposition, and also during gasification of fuel on hot plate or on flow of hot inert gas (at $\text{Re} = \text{const}$). Thus, according to [101], increase of pressure of nitrogen from 1 to 100 atm at 260°C practically did not change (and at 230°C only insignificantly increased) speed of thermal decomposition of NH_4ClO_4 . According to [113], increase of pressure of nitrogen from 1 to 7 [atm(abs.)] does not affect speed of pyrolysis w on hot plate. The same result was obtained (in the 1-26 atm interval) in work [233] for pyrolysis of NH_4ClO_4 on porous plate (in case of solid plate, speed of pyrolysis was increased with increase of pressure at assigned temperature of plate; however, this effect in work [233] is connected with methodical errors).

In case of diffusion burning of plate of polymer, rise in pressure, apparently, can noticeably increase speed of gasification (how temperature of surface of plate changes, was not investigated). Besides indirect data (increase in speed of burning out of liquids from free surface (see § 3B) and burning rate of drops (see § 4B) with increase in pressure) this is witnessed by the result obtained in work [124] for a plate of vinyl layer in contact with a layer of KClO_4 (see § 18). In the 10-40 atm range for linear speed of gasification (w), there was found $w \sim p^{0.2}$.

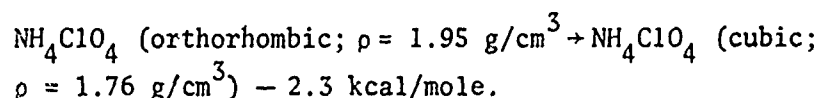
Finally, in case of burning of NH_4ClO_4 and NH_4NO_3 , when there is kinetic flame of products of decomposition near surface, speed of gasification $w = u$ strongly depends on pressure (see § 19). Moreover, in the region of high pressure there can be attained high values of w (so that, for NH_4ClO_4 at 1000 atm in work [121] there is obtained $w = u \approx 40$ mm/s). Data on dependence of surface temperature T_{Π} of burning charges on pressures are ambiguous:

for NH_4ClO_4 temperature rise of surface is noted with increase of pressure (however, data are reliable only at low pressures); on the contrary, for NH_4ClO_3 $T \neq f(p)$ (see below).

There are also other differences* in laws of gasification during slow thermal decomposition, in stationary wave of heating, and during burning of real mixtures. Nonetheless, comparative data on speed of gasification during slow thermal decomposition and also in stationary wave of heating, of course, are interesting with regard to the theory of burning of mixture systems.

Let us first consider the case of slow thermal decomposition of a suspension evenly heated to a certain (not too high) temperature, constant (or slowly increasing) in time. Speed of gasification in this case is defined as speed of liberation of gas (quantity of grams of gas per gram of suspension per unit of time). In practice arbitrary units are used: time of decomposition of a given percentage of substance at a given temperature; temperature at which in a given time there is decomposed a given percentage of substance, etc.

Real form of kinetic curves (degree of decomposition - time) can be very complex. It depends on temperature, presence of additions and contaminations; atmosphere in which experiment** is conducted, etc. In particular, the laws of decomposition of NH_4ClO_4 are greatly complicated by the presence of phase transition at 240°C :



Furthermore, at $T \lesssim 300^\circ\text{C}$ decomposition of NH_4ClO_4 takes place only partially, although remainder is identical with initial NH_4ClO_4 (see, for example, works [100, 101], in which there is a bibliography on the given question).

Consideration of real regularities of slow thermal decomposition is beyond the scope of this book. Let us consider only comparative data on total speed of gasification of different substances. For polymers there are similar data

*Thus, for example, in work [113] it is shown that addition of 3% $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ increases speed of slow thermal decomposition of NH_4NO_3 hundreds of times increases burning rate of compositions on the basis of NH_4NO_3 approximately twice but absolutely does not affect speed of pyrolysis of NH_4NO_3 on hot plate. Increase of molecular weight of polymer strongly affects speed of its gasification on heated plate, but weakly affects burning rate.

**Thus, for example, presence of oxygen strongly changes laws of thermal decomposition of polymers (see, for example, [129]). It is also not indifferent whether products of decomposition are removed or they are stored in the vessel where the experiment is conducted (in this case ratio of mass of substance to volume of vessel is important).

in works [99, 128] and others. The order in which polymers are disposed according to increase of their stability can depend on temperature (Fig. 17). However, many polymers can be simply disposed in a series according to their ability to gasify: the lightest of all is gasified polyformaldehyde, then comes polymethyl methacrylate, then come polyisobutylene and polystyrene, etc. The most thermoresistant is polytetrafluorethylene (teflon, polyfluoroethylene).

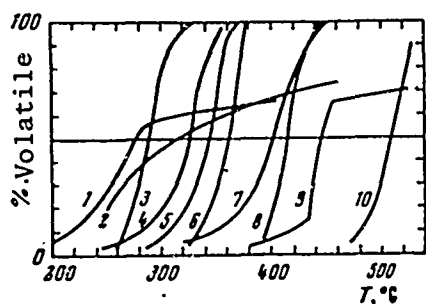


Fig. 17. Degree of gasification of polymers (% volatile with respect to initial polymers) during heating for 30 min, in vacuum at a definite temperature [128]
1 - polyvinylchloride; 2 - polyacrylonitrile;
3 - polymethylstyrene; 4 - polymethyl methacrylate; 5 - polyisobutylene;
6 - polystyrene; 7 - polybutadiene;
8 - polymethylene; 9 - polyvinylidene fluoride; 10 - polytetrafluorethylene.

We will now examine laws of gasification in stationary wave of heating. In this case, speed of gasification is defined as linear speed w of disappearance of condensed phase at a definite temperature T_{Π} on surface of layer of component. According to this determination, those substances are more easily gasified for which w is higher at given T_{Π} (or lower than T_{Π} at a given w).

We will stop at first on data on gasification in flow of hot gas and during heating from hot plate. There are a great number of works dedicated to ablation (i.e., taking away of mass) in gas flow. Not pretending to survey them, we will examine only a few works. We will be interested in the condition, in which ablation basically occurs at the expense of gasification.

In works [110, 111] ablation is studied of a number of uniform and reinforced plastics in flow of products of combustion of $C_2H_2 - O_2$ mixture at $\sim 3000^\circ C$ and 1 [atm(abs.)] [110] or air, heated in arc discharge (under conditions when enthalpy of air was 6600 BTU/lb $\approx$ 3670 cal/g, and heat flow to sample was 1500 BTU/ft²sec $\approx$ 360 cal/cm²·s [111]. Speed of gasification for teflon was 0.45 mm/s [110] or 0.89 mm/s [111] for nylon 0.51 mm/s [110]. Temperature on surface for teflon was 540°C [110] or $< 520^\circ C$ [111]; temperature was for nylon 1260°C [110].

In work [125] speed is measured of loss in weight $\dot{M}$ (g/s) of samples ($\phi 12.7$ mm, $h = 25.4$ mm) of plastics in city gas - oxygen flame ($T \approx 2500-3000^\circ C$):

Nylon	0.180	Polyethylene....	0.043
Polystyrene...	0.052	Graphite	0.001
Plexiglas.....	0.045		

For nylon and, to a lesser extent, for polystyrene and polyethylene, there is noted removal by flow of drops of melted polymer. Therefore, the figures given do not permit making a judgement about relative speed of gasification.

We measured speed of gasification (w , mm/s) of cylindrical samples ($\phi 10$ mm, $h = 12$ mm) of fuel in a charge torch ($\phi 60$ mm) of ballistite powder (at 1 [atm(abs.)]). The sample was armored from ends and rotated around its own axis with a speed of several revolutions per second (in avoidance of asymmetry of burning out and runoff of liquid drops for melted fuels). Speed of gasification (measured by loss of weight during time of experiment, which was 20-30 s) is very small:

Polystyrene	0.045	Polyformaldehyde ...	0.030
Plexiglas.....	0.022	Urotropine	0.035

For urotropine the value of w , apparently, is oversized, since small crystals of urotropine crack during fast heating.

There is a number of works [112-116, 233] and others), in which there is studied (usually at 1 [atm(abs.)]) gasification of samples of plexiglas, NH_4ClO_4 , NH_4NO_3 , NH_4Cl , pressed to hot plate.* Speed of gasification is measured by shift of sample. With the help of a thermocouple, temperature $T_{\text{ПЛАСТ}}$ is measured on surface of plate turned to sample (or on reverse side of plate [233]).

Value $T_{\text{ПЛАСТ}}$, with corresponding correction or without correction, is taken to equal temperature $T_{\text{П}}$ on surface of sample. In experiments on pyrolysis on solid plate between sample and plate, there is clearance through which products of gasification ebb sideways. Accordingly, there is a temperature gradient $\Delta T = T_{\text{ПЛАСТ}} - T_{\text{П}}$ between plate and sample.** This clearance could be removed to a considerable extent if one were to use a porous plate through which products of gasification were pumped.

For substances capable of independent burning (for example, NH_4ClO_4 , NH_4NO_3), at sufficiently high $T_{\text{ПЛАСТ}}$ there appears (between surface of charge and heated plate) a kinetic flame, and conditions of pyrolysis are absolutely changed (according to [233]; pyrolysis in the presence of burning can be studied only on a porous plate since for a solid plate in this case scattering of experimental points is very great).

In all studied cases, experimental points in coordinates $\ln w$, $1/T_{\text{П}}$ are grouped around a certain straight line, i.e., satisfy function:

$$w = Ae^{-E/RT_{\text{П}}}.$$

*In work 117] there was studied gasification of solid CO_2 on a hot plate.

**In work [114] there is given a rough estimate of $\Delta T = T_{\text{ПЛАСТ}} - T_{\text{П}}$ for pyrolysis of plexiglas:

w , mm/s	0.1	0.2	0.3	0.4	0.5
ΔT , °C	6	11.5	21	41	61

Table 32. Speed of Gasification of Different Substances on a Hot Plate

Substance	Structure of plate	Constant in equation $w = A \cdot e^{-\frac{U}{RT_n}}$		Temperature °C	Speed of gasification w, mm/s			Literature
		A, mm/s	U, kcal/mole		$T_n = 300^\circ \text{C}$	$T_n = 450^\circ \text{C}$	$T_n = 500^\circ \text{C}$	
Plexiglas	(wire)	$1.88 \cdot 10^7$	55	450-533		0.1	0.3	[112]
	Solid	$3.8 \cdot 10^4$	37 24-25	410-575 395-640	0.043	0.087 (445° C)	0.54	[113] [114]
NH ₄ ClO ₄	Solid	$3.4 \cdot 10^2$ 58, 8 · T _n	44 40	485-645			0.2 (510° C)	[109] [115]
	Porous		32 52° 29	400-640 <475 >475	0.02	0.045 (495° C)	0.5 (635° C)	[116] [233]
NH ₄ NO ₃	Substance	$1.2 \cdot 10^3$	11.2					[113]
NH ₄ Cl	Substance	23	29.4	330-640	0.01		0.03 (495° C)	[112]
	Porous		44	130-530	0.1 (370° C)		1.0 (495° C)	[116]

Approximately the same value is obtained and for a solid plate.

Values A and E for certain substances are given in Table 32. Data of different authors very greatly differ among themselves.

We will now examine gasification during diffusion burning of a layer of fuel in gaseous oxidizer. In work [122] there is studied burning out of channel in block of polymer at a given expenditure of oxygen through channel (w_{cp} was calculated by loss in weight during the time of burning τ). For plexiglas (at 1 [atm(abs.)]), $w_{cp} \approx 0.1$ mm/s, $T_{II} \approx 335-390^{\circ}\text{C}$ (value w_{cp} drops with increase in τ). Introduction into plexiglas of 0.25 or 0.5% soot, 30 or 60% aluminum, 30% titanium hydride does not change speed of gasification. Value w_{cp} for polyethylene is approximately the same as for plexiglas, but for polystyrene it is essentially higher (because of runoff of liquid drops).

In work [234] there is measured burning rate of plates (1" X 6" at thickness 1/2") of butyl rubber, polyurethane rubber and copolymer of butadiene and acrylic acid in flow of O_2 , F_2 and $\text{O}_2 - \text{F}_2$ mixtures. Value w for fluorine is higher than for oxygen, but approximately the same for the three polymers studied. In region of small flow rates of gas, value w strongly depends on flow rate and almost does not depend on pressure (apparanetly, diffusion region). Conversely, at high flow rates of gas, value w weakly depends on flow rate and strongly on pressure (apparently, burning passes into kinetic region). In particular, for burning of butyl rubber in oxygen and fluorine, there are obtained the following data:

p. atm	w. mm/s	
	in oxygen	in fluorine
1,75	0,155	0,34
4,2	0,28	0,66
8,4	0,42	0,90

In work [102] with the help of [IK-spectroscopy] (MK-spectroscopy), there is measured value T_{II} (in $^{\circ}\text{C}$) during burning of a number of polymers in air and oxygen:

Polymer	$T_{II}, ^{\circ}\text{C}$		Polymer	$T_{II}, ^{\circ}\text{C}$	
	in air	in oxygen		in air	in oxygen
Polyethylene . .	511	570	Polyurethan	had mon. tainite	507
Polyisobutylene	428	469	Plexiglas;	417	477-490

Gasification during burning on interface of layers of oxidizer and fuel is studied in work [124]. For system: layer of KClO_4 of thickness d between two thick plates of plexiglas, there is obtained value of speed of burning out of plexiglas (near "spout" flame) $w = 0.264$ mm/s for $d = 25$ mm, and $w = 0.218$ mm/s for $d = 3.8$ mm ($p = 1$ [atm(abs.)]).

Finally, we will stop on burning of NH_4ClO_4 and NH_4NO_3 in inert atmosphere. In this case gasification is carried out at the expense of heat transfer from kinetic flame of $\text{NH}_3 + \text{HClO}_4$ or $\text{NH}_3 + \text{HNO}_3$. Burning rate of NH_4ClO_4 and NH_4NO_3 essentially depends on pressure, initial temperature, presence of additions, density etc., i.e., on the same parameters as burning rate of homogeneous explosives (this is normal, since NH_4ClO_4 and NH_4NO_3 are weak [VV] (BB)). In § 19 functions $u(p)$, $u(T_0)$, etc., will be examined in detail for NH_4ClO_4 ; data will be given here about surface temperature $T_{\Pi} = f(u)$.

In work [108] for NH_4NO_3 with addition of 2.5% Cr_2O_3 , there is measured (with the help of a Pt - Pt Rh thermocouple) the value of surface temperature at different pressures. In the 140-280 atm range surface temperature practically did not depend on pressure (at 140 atm, $T_{\Pi} = 325$ and 316°C ; at 210 atm, $T_{\Pi} = 306$, 317 , and 285°C ; at 280 atm $T_{\Pi} = 313$ and 318°C). At the same time, burning rate essentially increased (from 4 mm/s at 140 atm to 8-9 mm/s at 280 atm).

Such a result absolutely does not agree with function $u = u = Ae^{-E/2RT_{\Pi}}$. Analogous data were obtained in this work for hydrazine nitrate and eutectic mixture of ammonium and hydrazine nitrates.

For NH_4ClO_4 value T_{Π} increased with increase in u , if u changes at the expense of increase of pressure:

p , atm	1*	21	35	71
T_{Π} , $^\circ\text{C}$	49 [102]	~51 [131]	~68 [130]	~72 [130]
u , mm/s	—	—	~30 [103, 104] 3-4	~50 [103, 104] 5-7

Values T_{Π} are measured by the IK-spectroscopy method and (according to [130]) are reliable only at $p \leq 4$ atm (since the given method can measure average temperature of a layer not less than 2 microns thick).

If burning rate grew at the expense of introduction of catalyst [102], then value T_{Π} not only did not increase, but even somewhat fell. There are

other data which do not agree with formula $u = Ae^{-E/2RT_{\Pi}}$. Thus, in work [106] value T_{Π} (measured with the help of thermocouples) drops with increase of pressure from $\sim 420^\circ\text{C}$ at 50 atm to $\sim 330^\circ\text{C}$ at 100 atm, although burning rate essentially rises. In work [131] value T_{Π} , measured for a number of compounds on the basis of NH_4ClO_4 , in limits of scattering remained constant during change of burning rate at the expense of change of pressure (in the interval

* At room temperature pure NH_4ClO_4 burns only at $p \geq 20-30$ atm. In order to carry out its burning at lower pressures, it was heated or additional fuel was mixed with it (value T_{Π} in both cases was the same). According to [102, 109, 130], value T_{Π} for mixtures with volatile fuels is the same as for pure NH_4ClO_4 .

1-15 atm), of particles of oxidizer or addition of catalyst.*

Finishing this division, we can come to the following conclusions.

1. In all cases studied temperature on surface of organic fuels, and also of oxidizers of the type NH_4ClO_4 , NH_4NO_3 , KClO_4 does not exceed 1000-1200°C, and is usually 400-700°C. Meanwhile, combustion temperature of mixture systems usually lies within the 2000-3000°C range (see, for example, [126]). Consequently, the temperature interval is sufficiently wide within limits of which components (or products of their decomposition) are in gas phase and can be energetically mixed.

2. At atmospheric pressure, speed of gasification of organic fuels does not exceed 1 mm/s both in the case where gasification occurs at the expense of heat addition from heated plate or flow of hot gas (case I), and in the case where plate of fuel burns in flow of gaseous oxidizer (case II):

Conditions of Gasification	w, mm/s
Burning of walls of channel through which oxygen flows	0.1-0.4
Burning of plate of fuel contacting plate of oxidizer	0.2-0.3
Ablation in flame of oxygen mixtures and flow of gas heated in arc discharge	to 1.0
Gasification on heated plate	to 0.5

However, with increase of pressure, apparently, there should appear difference between cases (I) and (II) (see above).

3. Function $w = Ae^{-E/2RT_n}$ well approximates experimental data only for pyrolysis on heated plate (but also here values of A and E measured by different authors for one and the same substance greatly differ). Under conditions of burning, this dependence can in no way be considered confirmed by experiment.

Let us also make a remark concerning the so-called "two-temperature theory of burning" of Schulz and Decker (see [97]). This theory: a) originates

from relationship $w = Ae^{-E/2RT_n}$; b) assumes that surface of charge has stationary form and c) consists of alternated flat "steps" of fuel and oxidizer.

For usual disordered systems, statement a) is not checked, and assumptions b) and c) knowingly are not fulfilled (burning is nonstationary and nonuniform in scale d, where d is dimension of particles of components).

* However, in work [130] the opinion is expressed that independence of temperature of surface from burning rate in work [131] and fall of surface temperature with increase of burning rate in work [106] do not reflect real curve $T_n(u)$ and are connected with errors of measurement, the more considerable the higher the burning rate.

D. Convective Mixing in Gas Phase

Till now we have assumed that mixing of components in the zone of heating and zone of reaction occurs especially at the expense of molecular diffusion. However, it is possible to assume that for mixtures with gasified components, a definite role can also be played by convection mixing [80].

We will examine causes which can lead to mutual introduction of volumes filled with products of gasification of components. To a number of such causes, there must first of all be related nonparallelism of flows of products of gasification of components, and also inequality of absolute values of speeds of flows.

Experience shows that at least at not too small a d , the surface of condensed phase turned to flame is not flat (see Fig. 18c), and along interfaces of components

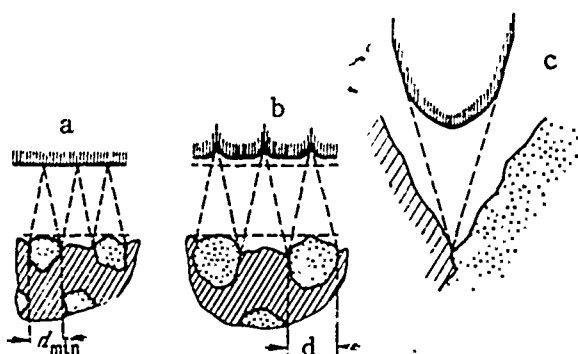


Fig. 18. Schematic appearance form of front of burning and surface of charge for condensed mixtures.
a) $d = d_{\min}$; b) $d > d_{\min}$, $d/d_{\min} \approx 1$; c) $d \gg d_{\min}$.

there will be formed wedge shaped cuts, which increase with increase in d . In direct proximity from the k -phase surface, products of gasification move perpendicularly to it due to the absence of any tangential forces. Therefore, direction of velocity vector of gas, $\vec{v}$, on surface changes from point to point, and near the surface there occurs collision of gas flows, which leads to their mixing.

For absolute values of speeds of products of gasification from condition of preservation of flow of mass for each of components, it is possible to write:

$$v_1 = \frac{\rho_1 w_1}{(\rho_1)_r}, \quad v_2 = \frac{\rho_2 w_2}{(\rho_2)_r}, \quad (45)$$

where ρ , ρ_r is density of condensed component and products of its gasification; w is speed of gasification (speed of disappearance of k -phase).

The time average values of $\bar{w}_1$ and $\bar{w}_2$ are proportional among themselves and are proportional to u , but current values w_1 and w_2 in any instant can be in an arbitrary ratio. Inasmuch as ρ_1 and ρ_2 , $(\rho_1)_r$ and $(\rho_2)_r$ are also in arbitrary ratio, then, in general $v_1 \neq v_2$.

Inequality of absolute values of speeds of products of gasification promotes their mixing in the tangential (perpendicular to $\vec{u}$) direction and makes possible convection mixing in the axial (parallel to $\vec{u}$) direction. Actually, we will examine the instant when at given point of surface, component 2 is replaced by component 1. Inasmuch as, in general, $v_{1a} \neq v_{2a}$, along the flow there should go either an elementary shock wave (at $v_{1a} > v_{2a}$), or an elementary wave of rarefaction (at $v_{1a} < v_{2a}$), which, being reflected from density heterogeneities existing in flow and from the k-phase surface, will produce gradually fading secondary, tertiary etc., wave. As a result, for example, at $v_{1a} > v_{2a}$ flow of gas 1 will be introduced into volume of gas 2, where the border between them will be eroded by pulsations of pressure and speed of gas appearing during passage of elementary waves.

It is essential, however, to emphasize that mixing of gas in the axial direction plays an insignificant role as compared to mixing in the tangential direction, since during gasification of a small cube of solid component, there will be obtained a rectangular volume of gas, for which dimensions of base were not changed, when height (and together with it path of mixing in axial direction) was increased ρ/ρ_p times (i.e., in usual conditions one-three orders).

Existence of turbulent mixing of the type examined in the end is connected with the fact that the initial condensed mixture itself with disorderly location and form of particles constitutes a kind of "frozen" turbulence, which "revives" during gasification of components. Consequently, we are concerned with artificially created turbulence, similar to that which appears during the work of different mixers, etc. This form of turbulence does not have direct connection with parameters (and, in particular, with the value of Re) of steady flow of products of gasification and combustion. The level of artificially created turbulence is the highest near the surface of the condensed phase (k-phase), i.e., exactly in that zone which usually renders the biggest influence on burning rate. Further along the flow, artificially created turbulence fades. The basic scale of turbulence in this case should be proportional to d .

For the artificially created turbulence examined, we dispose one parameter with dimension of length d and one parameter with dimension of speed $\vec{v}_1 - \vec{v}_2$, from which it is possible to compose a combination having the dimension of coefficient of turbulent exchange (cm^2/s):

$$D_{\text{type}} \sim d(v_1 - v_2), \quad (46)$$

for mixing in the tangential direction, one should take $v_{1t} - v_{2t}$, and for mixing in the axial direction, one should take $v_{1a} - v_{2a}$.

Putting (45) into (46) and considering $u_1 \sim u_2 \sim u$, we will obtain:

$$D_{\text{type}} \sim u d \rho' \rho_r \sim \frac{u d}{p}. \quad (47)$$

We will consider now that coefficient of molecular diffusion $D \sim 1/p$ and does not depend on d , and also that usually $u \sim p^2$, where $v > 0$. It follows from this that the role of convection mixing increases according to increase in d and p . It should increase also according to distortion of k -phase surface, inasmuch as angle of collision of streams is increased and inasmuch as the path of mixing in the tangential direction is much less than in the axial direction.

Formula (47), of course, still does not make it possible to estimate for a given system the value of d starting from which convection mixing becomes comparable with molecular mixing, since there are absent any considerations about value of numerical proportionality factor in the right part (47). For qualitative check of expounded considerations on role of convection mixing, Yu. V. Frolov and we set up experiments, in which with the help of movie camera with a set of light filters, there was determined height, n of nucleus of torch of cylindrical charges ($\phi = 1$ cm) of $KClO_4$ - bitumen mixture with dimension of $KClO_4$ particles of $d \approx 10, 180$ and 1700 microns. Spray combustion occurred inside a large vessel filled with nitrogen at 1 [atm(abs.)] and $20^\circ C$. It was found that height of nucleus of torch not only did not increase, but, on the contrary, somewhat decreased during transition from $d \approx 10$ microns to $d \approx 1700$ microns, which talks in favor of increase in mass exchange coefficient with increase in d .

Function $h(d)$ was also determined for the case of burning of a separate "particle." For this, powdery $KClO_4$ is pressed into thick cylindrical plexiglas shells with different internal diameters (from 0.4 to 1.5 cm). Let us note that in this case one should consider $\phi = d$. From considerations of dimension it follows that:

$$h \sim v d^2 / D \sim u d^2 / \rho_f D, \quad (48)$$

where for the system examined, u almost does not depend on d [127]. Therefore, for molecular mixing, there should be fulfilled $h \sim d^2$. Conversely, if mixing is turbulent ($D_{\text{turb}} \sim d$), then $h \sim d$.

The experiments conducted showed that in every given experiment, value h noticeably oscillated from frame to frame near a certain mean value. The latter remained constant during a considerable part of the time of burning for $d = 4-10$ mm and for $d = 15$ mm, it decreased with burning out of charge. For the mean value of h_{cp} there was obtained:

$d, \text{ mm}$	4	6	10	15
$h_{cp}, \text{ mm}$	10	19	49	60

At coordinates ($\lg h_{cp}$, $\lg d$) these points are disposed near a straight line corresponding to function $h_{cp} \sim d^{1.3}$, which also argues in favor of the presence of convection mixing.

§ 7. Certain Regularities of Transfer of Particles and Drops by Gas Flow

For a majority of pyrotechnic mixtures, oxidizer is gasified considerably more easily than fuel. Particles of fuel are attracted by flow of products of gasification of oxidizer and burn in suspension above surface of charge. Transfer of particles of fuel and oxidizer by gas flow can take place for systems with organic fuels. Particles of fuel and oxidizer in flow can assist particle of condensed residue formed during decomposition of initial components (for example, KCl) or during their burning (for example, MgO, Al_2O_3 etc.).

There is very extensive and various literature dedicated to regularities of flow of two-phase media (solid particles — gas or liquid drops — gas). However, we will be interested only in certain elementary relationships for two phase flow, which are useful for understanding processes affecting burning rate of condensed mixtures. Accordingly, we will examine motion of particles only near surface of charge, not touching on the question of outflow of two-phase media through nozzle, etc.

A. Maximum Cases of Sufficiently Small and Sufficiently Big Particles

For understanding regularities of burning of particles near surface of charge, it is very useful to isolate cases "of sufficiently small" and "sufficiently big" particles.

We will call sufficiently small a particle for which time of acceleration of particle to speed close to speed of gas is much less than time of stay in zone affecting burning rate ("zone of influence").

We will call sufficiently big a particle which is practically stationary with respect to charge or moves with speed much less than speed of gas.

If one passes now to a system of coordinates combined with front of burning and designates particle speed by x and speed of gas by v , then within limits of zone of influence for a sufficiently small particle, $x \approx v$, and for a sufficiently big particle $x \approx u$, where u is burning rate.

In order to estimate the dimension, "sufficiently small" and "sufficiently big" particle, it is necessary to dispose information, first, about dimension of zone of influence and, secondly, about law of particle motion. We will examine the question of zone of influence in greater detail in § 10B; however, it is necessary to note immediately that quantitative information about dimension of zone of influence is extremely scanty. It is clear only that width of zone of influence does not exceed several millimeters and is reduced with increase of pressure. Conversely, with increase of dimension of particles of components, width of zone of influence, apparently, increases.

Let us estimate dimensions "of sufficiently small" and "sufficiently big" particles for the special case when: 1) there is a single particle, which at time $t = 0$ suddenly starts to be blown by a flow of gas; 2) force

having effect on particle from the side of gas flow F_1 can be found by the formula of Stokes;* 3) besides F_1 only gravity acts on particle.** Problem formulation usual for laboratory conditions is examined when charge burns down from above.

Let us note that these limitations do not affect the basic idea about presence "of sufficiently small" and "sufficiently big" particles (only appraisals of dimension of such particles change).

In the special case examined particle motion will be described by equation:

$$\frac{\pi}{6} d^3 \rho \ddot{x} = 3\pi d \eta (v - \dot{x}) - \frac{\pi}{6} d^3 \rho g, \quad (49)$$

where d , ρ are diameter and density of particle; η is viscosity of gas; g is acceleration of gravity.

Equating right side of equation (49) to zero, we will obtain appraisal of dimension of "sufficiently big" particle:

$$d_* = \sqrt[3]{\frac{18\eta(v-u)}{\rho g}}. \quad (50)$$

Such appraisal ($d \geq d_*$) is appraisal from above, since particles somewhat smaller than d_* will accelerate so slowly that within limits of zone of influence for them it is practically the case that $x \approx u$.

For $d \leq d_*$ integrating (49) during initial conditions $x|_{t=0} = 0$ and $\dot{x}|_{t=0} = u$, we will obtain:

* In general the expression for F_1 is usually recorded in the form $F_1 = C_x \cdot \frac{1}{2} \rho_r (v - \dot{x})^2 \pi d^2 / 4$. At small values of Re , when the formula of Stokes is valid, dimensionless drag coefficient $C_x = 24/Re$. With increase in Re , experimental value C_x becomes larger (see, for example [32]):

Re	0.1	1.0	10	100
$C_x = 24/Re$	240	24	2.4	0.24
$(C_x)_{\text{exper}}$	245	28	1.4	1.1

** Experimental data (mainly on burning of particles of metals) indicate that, apparently, there exist also cohesive forces between particles and surface of charge (if there is a melted layer, then the particle is held by forces of surface tension and viscous forces). This question up to now, has been investigated almost not at all.

$$x = u + \left(v - u - \frac{\rho d^2}{18\eta} g \right) (1 - e^{-18\eta t / \rho d^2}), \quad (51)$$

$$x = \left(v - \frac{\rho d^2}{18\eta} g \right) t - \frac{\rho d^2}{18\eta} \left(v - u - \frac{\rho d^2}{18\eta} g \right) (1 - e^{-18\eta t / \rho d^2}). \quad (52)$$

Putting $t \rightarrow \infty$ into (51) or equating the right part of (49), to zero we will obtain value of uniform velocity of particle $v = v - \frac{\rho d^2}{18\eta} g$. For very small ($d \rightarrow 0$) particles, $x \approx v$.

From (51) and (52) it is easy to find time t_k and length of path x_k , which are necessary* so that particle obtain speed equal to $0.9x$ (for example, $0.9x$). Let us give numerical example for products of gasification of usual mixture system (we will take $u|_{1\text{atm}} = 1 \text{ mm/s}$, $u|_{100\text{atm}} = 10 \text{ mm/s}$, $T \approx 100^\circ\text{C}$, $\mu = 40$, $\eta \approx 4 \cdot 10^{-4} \text{ g/cm}\cdot\text{s}$, $\rho = 2 \text{ g/cm}^3$). For length of section on which particle will succeed in accelerating to a speed of $0.9x$ (microns), we will obtain:

d, micron	$x_k \approx 0.9 \cdot \text{micron}$		d, micron	$x_k \approx 0.9 \cdot \text{micron}$	
	$p = 1$ [atm(abs.)]	$p = 100 \text{ atm}$		$p = 1$ [atm(abs.)]	$p = 100 \text{ atm}$
0,1	0,16	0,016	10	16,00	160
1	16	1,6	100	15,4 cu	—

In practice, apparently, particles smaller than one micron can be considered "sufficiently small" particles. Particles ~ 100 microns and above are clearly "big."

It is also of interest to estimate time of heating t_{nporp} of particle up to temperature of gas. Value t_{nporp} is limited by heat transfer from gas to particle. Let us define t_{nporp} in the following way. Let us assume that $t = 0$, a spherical particle with temperature T_{II} gets into flow of gas with temperature T_{I} . For brevity we will examine only the case when particle does not melt and essentially does not evaporate at $T \leq T_{\text{I}}$ and when temperature in different points of particle changes equally in time. Let us take t_{nporp} equal to that interval of time during which difference between temperature

*Let us note that in work [136] it was erroneously accepted that $C_x = \text{const}$ (this is valid only at $\text{Re} \approx 2 \cdot 10^3 - 10^5$, but not those small Re , which are characteristic for conditions interesting us). As a result, values x_k and t_k in that work turned out to be greatly overestimated.

of particle and gas will decrease e times (from $T_F - T_{II}$ to $T_F - T_*$ = $(T_F - T_{II})/e$). Let us record equation of heat balance:

$$\pi d^2 \alpha' (T_F - T) \partial t = \frac{\pi}{6} d^3 \rho c \partial T, \quad (53)$$

where α' is coefficient of heat transfer; c is heat capacity of particle.

Integrating (53) at initial condition $T|_{t=0} = T_{II}$, we will obtain:

$$t = \frac{\rho c d}{6 \alpha'} \ln \frac{T_F - T_{II}}{T_F - T_*}. \quad (54)$$

For small spherical particles, $\alpha' = Nu \frac{\lambda_F}{d} \approx 2 \frac{\lambda_F}{d}$.

Putting value α' , into (54) and also $T_* - T_{II} = (T_F - T_{II})/e$, we will obtain:

$$t_{\text{нпогр}} \approx \frac{\rho c d^2}{12 \lambda_F} = \frac{1}{12} \frac{d^2}{a} \frac{\lambda_F}{\lambda_F}, \quad (55)$$

i.e., time of heating of small spherical particle ($Nu = 2$)* is proportional to square of its diameter, proportional to ratio of coefficients of thermal conduction of particle and gas** and inversely proportional to coefficient of temperature transfer of gas.

Value $t_{\text{нпогр}}$ for small particles yields well to numerical appraisal, since product ρc for inorganic salts, polymers and metals lies approximately in the same interval (for substances interesting us, $\rho c = 0.3-0.7$ cal/cm³·deg), where ρc weakly depends on temperature. Taking $\lambda_F \approx (2-4) \cdot 10^{-4}$ cal/cm·s·deg (see, for example, [132]), we will obtain for time of heating of small particles (indifferently — of fuel, oxidizer or metal) the following appraisal:

$d, \text{microns} \dots\dots$	0.1	1	10
$t_{\text{нпогр}}, \text{s} \dots\dots$	$(0.3 \div 0.7) \cdot 10^{-4}$	$(0.3 \div 0.7) \cdot 10^{-3}$	$(0.3 \div 0.7) \cdot 10^{-2}$

*In work [133] is led empirical formula for Nu during flowing around of sphere

$$Nu = 2 + 0.03 Pr^{0.31} Re^{0.31} + 0.35 Pr^{0.31} Re^{0.31}$$

At $Re = 1$ (and $Pr \approx 1$), value $Nu \approx 2.4$ is still close to $Nu = 2$. Under conditions of burning, value $Re < 1$ corresponds at 1 [atm(abs.)] to particles less than ~10 microns, and at 100 atm it corresponds to particles under ~1 micron.

**Consequently, time of heating of particle (limited by heat transfer from gas to particle) exceeds time of temperature balance inside particle (proportional to d^2/a) λ/λ_F times (for example, for particles of metals by approximately three orders).

Time of heating of small particle is of the same order or one and a half orders less than time of acceleration of particle to uniform velocity.

Time of heating of big particles (especially taking into account distribution of temperature inside particle) does not yield to elementary appraisal and within the bounds of the present work, we will not examine it.

B. Parameters of Two-Phase Flow

It is of interest to obtain an expression for number of particles, and also mass of particles and gas in a unit of volume of two-phase flow for average heat capacity and thermal conduction, etc., (part of these expressions is extracted in work [134] and — in another form — in work [135]).

For simplicity of recording, we will examine a system in which oxidizer is completely gasified and fuel is nonvolatile and burns in flow of products of gasification of oxidizer. Let us introduce the following symbols:

	Condensed mixture (k-phase)	Two-phase flow
Density in g/cm^3		
of oxidizer	ρ_{ok}	ρ_{Γ}
of fuel	ρ	ρ
average	$\bar{\rho}$	$\bar{\rho}'$
Part of fuel		
weight in g/g	x	x'
volume in cm^3/cm^3	V	V'
Part of area of cross section occupied		
by particles of fuel, cm^2/cm^2	S	S'
Number of particles of fuel in 1 cm^3	n	n'
Speed (with respect to front of burning), cm/s		
particles	u	x
gas	—	v
Heat capacity $\text{cal/g} \cdot \text{deg}$		
oxidizer	c_{ok}	c_{Γ}
fuel	c	c
average	$\bar{c}$	$\bar{c}'$
Thermal conductivity in $\text{cal/cm} \cdot \text{s} \cdot \text{deg}$		
of oxidizer	λ_{ok}	λ_{Γ}
of fuel	λ	λ
average	$\bar{\lambda}$	$\bar{\lambda}'$

From the number of these values, we will consider assigned all values belonging to the k-phase, and also $\rho_r = p_0/RT$ and x , which we consider only in the two maximum cases: for sufficiently large particles $x = u$ and for sufficiently small particles, $x = v$. Let us note also expressions for $\bar{\rho}$, V , S and n through other parameters of the k-phase:

$$1/\bar{\rho} = \chi/\rho + (1 - \chi)/\rho_{0k} \quad (56)$$

$$V = S = \chi \cdot \bar{\rho}/\rho \quad (57)$$

$$n = 6V/\pi d^3 = 6\bar{\rho}/\rho \pi d^3. \quad (58)$$

We will now record the equation of preservation of flow of mass for that section of flow where particle of fuel are accelerated by gas and are heated, but still do not succeed in essentially burning. In this case flow of mass of particles and flow of mass of gas will be preserved separately:

$$\bar{\rho} \chi u = \rho S u = \bar{\rho}' \chi' x = \rho S' x \quad (59)$$

$$\bar{\rho} (1 - \chi) u = \rho (1 - S) u = \bar{\rho}' (1 - \chi') v = \rho (1 - S') v \quad (60)^*$$

From (59) and (60) we will obtain:

$$V' = S' = V \frac{u}{x} = S \frac{u}{x}, \quad (61)$$

$$n' = \frac{6V'}{\pi d^3} = n \frac{u}{x}. \quad (62)$$

For big particles ($x \approx u$) the portions of volume and area of cross section of flow occupied by particles are equal to corresponding values in k-phase (particles of fuel will form a fixed grid through which gas flows). Conversely, for the case of small particles ($x \approx v$) the part of volume and area of cross section of flow occupied by particles is much less than in k-phase, since the same number of particles which in k-phase consisted in a cylinder of height u in two-phase flow consists in a cylinder of height v , where $v \gg u$.

For average density of substance (quantity of grams of gas and particles in 1 cm^3 of flow), we will obtain:

$$\bar{\rho}' = \frac{\chi \bar{\rho} u}{x} + \frac{(1 - \chi) \bar{\rho} u}{v}. \quad (63)$$

The first member in the right part of equation (63) corresponds to mass of particles in 1 cm^3 of flow; the second member corresponds to mass of gas in 1 cm^3 of flow. For big particles ($x \approx u$) the first member (and together

*Let us note that in work [136], the left part of equality (1'), analogous to equation (60), is written inaccurately (it is valid only at $x = v$ and $\rho = \bar{\rho}$).

with it $\bar{\rho}'$) is very large as compared to the second, since mass of big particles in 1 cm^3 of flow is the same as in 1 cm^3 of the k-phase. The second member in this case can be disregarded ($u/v \ll 1$), so that $\bar{\rho}' \approx \chi \bar{\rho}$. In other words, in this case mass of particles in 1 cm^3 of flow is very great as compared to mass of gas in 1 cm^3 of flow.

For small particles ($\chi \approx u$), equation (63) takes on trivial form

$$\bar{\rho}' v = \bar{\rho} u.$$

Ratio of mass of small particles and of mass of gas

$$\frac{\chi \bar{\rho} u/v}{(1-\chi) \bar{\rho} u/v} = \frac{\chi}{1-\chi}$$

is the same as in k-phase. This means that mass of small particles in 1 cm^3 of flow is proportional to density of gas ρ_T , and, consequently, is proportional to pressure.

It is necessary to note that at predetermined speed of burning u and assigned density of gas ρ_T speed of gas v in two-phase flow determined from (60):

$$\rho_T v = \rho u \frac{1-S}{1-S'}, \quad (64)$$

will be lower than in single-phase flow, where it would be determined from relationship:

$$\rho_T v = \rho u. \quad (65)$$

Indeed

$$\frac{1-S}{1-S'} = \frac{1-S}{1-S' \frac{u}{\chi}} < 1,$$

since $\chi \geq u$ (only for big particles, when $S' = S$, (64) gives the same value for v as (65)). The meaning of this result is obvious; in two-phase flow, particles occupy a smaller fraction of cross section than in k-phase, but gasified component, accordingly, occupies a larger fraction. In the limit (at $[1-S' \frac{u}{\chi} \rightarrow 1]$) speed of gas in two-phase flow is $1-S$ times lower than in single-phase flow.

It is also useful to write an expression for part by weight χ' of particles in two-phase flow (mass of particles per unit of mass of substance of flow):

$$\chi' = \frac{1}{1 + \frac{1-\chi}{\chi} \frac{u}{v}} \quad (66)$$

For small particles $\chi' = \chi$, i.e., part by weight of small particles in two-phase flow is the same as in k-phase. In the remaining cases, $\chi' > \chi$. In particular, for big particles, $\chi' \rightarrow 1$ (these results for small and big particles were already noted by us in examining formula (63)).

Heat capacity for two-phase flow is equal to:

$$c' = \chi'c + (1 - \chi')c_r \quad (67)$$

In the case of big particles ($\chi' \rightarrow 1$), heat capacity so practically equal to heat capacity of particles $\bar{c}' \simeq c$.

There are only approximate formulas for coefficient of thermal conduction of mixtures of two components. In particular, it is possible to use the formula of Maxwell, which for the case of two-phase flow interesting us will be recorded in the form:

$$\bar{\lambda}' = \lambda_r \frac{2\lambda_r(1 - V') + \lambda(1 + 2V')}{\lambda_r(2 + V') + \lambda(1 - V')} \quad (68)$$

or formula for average geometric value:

$$\bar{\lambda}' = \lambda_r^{1-V'} \lambda^{V'} \quad (69)$$

For small particles, $V' \rightarrow 0$ and, therefore, $\bar{\lambda}' \simeq \lambda_r$, i.e., presence of small particles has almost no effect on thermal conduction.

During large dimensions of particles, formulas of type (68) and (69) can hardly be used, since in this case an essential role can be played by heat exchange at the expense of convection of gas and radiation, which is not considered in these formulas.

§ 8. Kinetic and Diffusion Conditions of Burning Certain Expressions for Burning Rate

Burning rate of condensed mixtures, in general, depends both on kinetic and on diffusion* factors. However, there is a number of cases, when only kinetic or only diffusion factors are determining factors.

*Diffusion factors here and below will imply factors connected with speed of mixing of fuel and oxidizer, but not with rate of diffusion of products of combustion into fresh mixture (as this was considered in § 1).

A. Kinetic Conditions of Burning at Sufficiently Small Dimension of Particles of Components

If processes of mixing are completed within limits of zone of heating (i.e., before the beginning of reaction), they will not affect burning rate. Obviously, in this case burning takes place in kinetic conditions, but burning rate does not depend on dimension of particles of components and should equal burning rate of homogeneous system of the same chemical composition. Such conditions of burning were examined for the first time in work [127], and then more specifically, in work [81].

In division A § 6 it was already noted that mixing in zone of heating can occur only under the condition that fuel and oxidizer (or products of their destruction) possess sufficient mutual solubility and that this condition is knowingly satisfied for system $\Gamma + \Gamma$ and is not satisfied for systems $\Gamma + \text{TB}$ and $\Gamma + \text{Ж}$ (in cases $\text{TB} + \text{TB}$, $\text{TB} + \text{Ж}$, $\text{Ж} + \text{Ж}$, the possibility of mixing components can be estimated only for concrete system).

Examined conditions can be observed only at sufficiently small d (at $d \leq d_{\min}$). The value of d rises with increase of diffusion rate and is limited from below, since it, in any case, should exceed effective dimension of molecules:

$$d_{\min} > 10^{-8} \div 10^{-7} \text{ cm.} \quad (70)$$

Consequently, the second condition of existence of examined conditions is not too small a speed of mutual diffusion of components (a speed which satisfies condition (70)).

Departing from considerations given in work [127], we will watch for mutual diffusion of components in certain section ($x = 0$) of charge. During the time ∂t , border of zone of mixing will shift in transverse direction by value of order:

$$\partial(y^2) \sim D \partial t. \quad (71)$$

Assuming that front of burning moves relative to given section with constant speed, u , we can write $x = x' - ut$, where x' is reckoned from front of burning. Using known expression for profile of wave of heating before front of burning,

$$x' = \frac{a}{u} \ln \frac{T - T_0}{T_r - T_0}, \quad (72)$$

where a is temperature transfer in cm^2/s , and where temperatures T_0 and T_r pertain to cold mixture and zone of reaction, respectively, after substitution of $\partial t = \partial x'/u$ into (71) and integration, we will obtain that $d_{\min}$ in order of magnitude equals:

$$d_{\min} \sim \frac{1}{m} \sqrt{\frac{\lambda}{c} \left[\int_{T_0}^{T_r} \frac{\rho D}{T - T_0} \partial T \right]^{1/2}}, \quad (73)$$

where m is mass burning rate (at $d \leq d_{\min}$), $\text{g/cm}^2 \cdot \text{s}$; ρ is density in g/cm^3 ; for values $\bar{\lambda}$ ($\text{cal/cm} \cdot \text{s} \cdot \text{deg}$) and $\bar{c}$ ($\text{cal/g} \cdot \text{deg}$) there are taken values which are average for the preparatory zone. If in the latter there take place phase transitions, then it is split into several subzones, and integration in (73) is conducted in series for each of them. For brevity let us assume that mixing takes place basically in one subzone, lying in the interval from T_1 to T_r (where $T_0 < T_1 < T_r$). For mutual diffusion of gases, there is usually taken $D = D_0(T/T_0)^n$, where $n = 1.75-2$. At $n = 2$ we will obtain from (73):

$$d_{\min} \sim \frac{1}{m} \sqrt{\frac{\bar{\lambda} \bar{\rho} D_0}{\bar{c}}} \sqrt{\frac{T_r - T_1}{T_0} + \ln \frac{T_r - T_0}{T_1 - T_0}}. \quad (74)$$

For diffusion in solid and liquid phases, $D = D_* e^{-Q/RT}$, and then from (73) it follows that:

$$d_{\min} \sim \frac{1}{m} \sqrt{\frac{\bar{\lambda} \bar{\rho}}{\bar{c}}} D_* \cdot \left\{ \text{li}(e^{-Q/RT_1}) - \text{li}(e^{-Q/RT_r}) + e^{-Q/RT_*} [\text{li}(e^{Q/RT_*} e^{-Q/RT_r}) - \text{li}(e^{Q/RT_*} e^{-Q/RT_1})] \right\}^{0.5}. \quad (75)$$

Values $\text{li } z$ taken from tables; however at $Q \gg RT$ (approximately, at

$e^{-Q/RT} < 10^{-4}$, $e^{Q/RT}$, $e^{-Q/RT} > 10^4$) with error not more than 10-12% it is possible to

use approximation $\text{li } z \approx z/\ln z$. If furthermore $e^{-Q/RT_r} \gg e^{-Q/RT_1}$, is fulfilled then from (75) we will obtain:

$$d_{\min} \sim \frac{1}{m} \sqrt{\frac{\bar{\lambda} \bar{\rho}}{\bar{c}}} \sqrt{D_* \frac{RT_r}{Q} e^{-Q/RT_r}}. \quad (76)$$

Formulas (74)-(76) in principle permit estimating $d_{\min}$ for every concrete system.

It is of interest to estimate the interval in which value $d_{\min}$ can lie for a given type of systems. This succeeds well for variant $\Gamma + \Gamma$. The fact

is that value of complex $\theta = \sqrt{\frac{\bar{\lambda}}{\bar{c}} \rho_0 D_0}$ for all gases which can be products of

gasification of different condensed mixtures and for which there are tabular data changes in comparatively narrow limits; thus, for example, in interval

$\theta = 10^{-4} - 10^{-3} \text{ g/cm} \cdot \text{s}$, we will get all the usual diatomic and triatomic gases, different gaseous hydrocarbons, including very heavy vapors of many organic liquids, etc., (at temperatures from 200-300°C; it is accepted that $T_0 = 273^\circ\text{K}$).

Furthermore, if one does not examine function $m(p, T)$, which comes from experiment,

then right side of formula (74) does not depend on pressure and comparatively weakly depends on selection in reasonable limits of temperatures T_{Γ} , T_1 and T_0 . Taking, for example, that temperature T_{Γ} and T_1 can independently change in intervals 1500-3000 and 600-1000°K, respectively, we obtain from formula (74) the following interval of values $d_{\min}$:

$$d_{\min}(\mu\kappa) \approx \frac{1.5 + 3.5}{m(g/cm^2 \cdot s)} \quad (77)$$

In work [137] the experimental value of $d_{\min}$ for stoichiometrical mixture of $KClO_4$ + bitumen at $m \approx 0.2 g/cm^2 \cdot s$ was 70 microns, which lies within estimated limits (77).

The matter is much worse for variants $\kappa + \kappa$, $TB + \kappa$ and especially $TB + TB$, since some data are absent on diffusion in systems of metal + salt, resin + salt, etc. Indirect data (diffusion of metals in metals and slag, mutual diffusion of salts, etc.) show that for $TB + TB$ system, coefficient of diffusion extraordinarily strongly depends on nature of components, and this excludes possibility of any estimates of $d_{\min}$ by indirect data. For diffusion in liquid phase, dependence on nature of components is considerably weaker; however, the interval of values $d_{\min}$, which give indirect data, being placed in (75) (in reasonable assumptions with respect to range of charge of T_1 and T_{Γ}) nevertheless is about four orders. Such a wide estimate is of no practical interest.

B. Diffusion Conditions of Burning of Suspensions of Solid Particles

In the preceding division (§ 8A), we noted that for a system of the type $\Gamma + TB$ or $\Gamma + \kappa$, there cannot be carried out kinetic conditions connected with mixing of components in zone of heating, and that for these systems, mixing can take place only simultaneously with burning.

However, for $TB + \Gamma$ (or $\kappa + \Gamma$) systems, there can take place purely diffusion (and, in principle, also purely kinetic) conditions combined with the fact that burning of every particle (or drop) takes place in the diffusion (or kinetic) region.

Here we will examine only diffusion conditions, since kinetic conditions, apparently, have not been carried out by experiment.

O. I. Leypunskiy [65] proposed to examine burning of suspension of solid particles as burning of homogeneous gas mixture, where in accordance with the theory of Ya. B. Zel'dovich, it was accepted that

$$m \sim \sqrt{\phi}, \quad (78)$$

where m is mass burning rate in $\text{g/cm}^2 \cdot \text{s}$; ϕ is speed of liberation of heat per unit of volume of two-phase flow (solid particles + gas), $\text{cal/cm}^3 \cdot \text{s}$.

Such assumption is basic for the case of sufficiently small particles (this case, namely, was examined in work [65]). For big particles the applicability of formula (78) becomes doubtful; however, for want of better founded relationships it is nevertheless necessary to use this formula for qualitative results.

Heat emission at the expense of burning of particles can be written in the form (see [138]):

$$\phi = \rho \frac{\partial r}{\partial t} \pi d^2 n' Q, \quad (79)$$

where ρ is density of particle, g/cm^3 ; $\partial r / \partial t$ is speed of its burning in cm/s ; $2r = d$ is particle diameter in cm ; n' is the number of particles in 1 cm^3 of two-phase flow; Q is the heat of burning per gram of fuel in cal/g .

Substituting $\frac{\partial r}{\partial t} = \frac{1}{r_0} (N + L)$ from (39) and n' from (62), we obtain for mass flame propagation velocity (from 78):

$$m \sim \frac{1}{d} \sqrt{12(N + L) Q \chi \frac{\bar{p}}{\rho} \frac{u}{x}}. \quad (80)$$

If one is interested only in dependence of burning rate on pressure and dimension of particles (80) can be rewritten in the form:

$$m \sim \frac{1}{d} \sqrt{\frac{u}{x}}. \quad (81)$$

since all remaining values under the radical in (80) do not depend on pressure (N , Q , χ , $\bar{p}$, ρ) or almost do not depend (L) on pressure.

For small particles, $x \approx v \sim \rho u / \rho_f$ and accordingly $u/x \sim \rho_f \sim p$. Thus, for flame propagation velocity in suspension of small solid particles (or liquid drops) in the case when burning of particle takes place in diffusion conditions, we will obtain:

$$m \sim \sqrt{p/d} \quad (82)$$

(which coincides with formula (4) in work [65]).

For big particles (burning in diffusion conditions), it follows from (81) that:

$$m \sim 1/d \neq f(p) \quad (83)$$

Consequently, flame propagation velocity in suspensions of solid particles depends on pressure, for small particles, but does not depend on pressure for big particles. Meanwhile burning rate and time of burning of every separate particle (whether small or big) in diffusion conditions does not depend on pressure (see § 4A). However, the number of small particles in 1 cm^3 of flow is proportional to pressure, but the number of large particles in 1 cm^3 of flow does not depend on pressure (see (62)). This leads to $m \sim \sqrt{p}$ for a suspension of small particles and $m \neq f(p)$ for a suspension of big particles.

At the conclusion of (80) and (81), no assumptions were made about whether particles are volatile or nonvolatile (the laws of diffusion burning do not depend on volatility, only the ratio r_ϕ/r_k changes and, accordingly, absolute value of burning rate changes; see § 4A). However, experimental data given in Chapter III show that for mixtures with easily gasified components (to which there belong such oxidizers as NH_4ClO_4 , KClO_4 , NH_4NO_3 and the majority of organic fuels) dependence $u(d)$ is weak and has nothing in common with $u \sim m \sim 1/d$.

Only for nonvolatile fuels (for example, graphite and tungsten) is dependence $u(d)$ strong and does it approach $u \sim m \sim 1/d$ (see § 13).

Besides function $u(d)$ it is also necessary to examine whether theoretical function $u(p)$ agrees with experiment. According to the formula (82) and (83), function $u(p)$ should be weakened during transition from small to big particles. However, in work [139] for $\text{Al} - \text{Fe}_2\text{O}_3$ and $\text{W} - \text{KClO}_4$ mixtures, exactly the reverse effect is revealed: burning rate depended on pressure more for coarsely dispersed mixtures than for finely dispersed mixtures (see Table 41).

This divergence can be connected with the fact that it is not at all necessary for burning of particles to take place in free gas flow. Accordingly, the theoretical dependence $u(p)$, described by formulas (82) and (83) is not possible only for diffusion burning.

In work [140] the case is examined when gasification of oxidizer is accompanied by formation of condensed residue (for example, $\text{KClO}_4 \rightarrow \text{KCl} + 2\text{O}_2$ or $\text{Fe}_2\text{O}_3 \rightarrow 2\text{Fe} + 1.5\text{O}_2$) or when part of products of reaction at a temperature of burning are liquid or solid. In this case the condensed remainder holds particle of fuel from removal by gas, forming a more or less dense layer through which bubbles and streams of gas break.

In this case particles (both small and big) are stationary relative to fresh substance $x \approx u$. Accordingly, the number of particles in 1 cm^3 of flow is constant at all pressures and equal to the number of particles in 1 cm^3 of initial mixture. However, value N from (80), in general, can depend on pressure, since diffusion does not necessarily take place in free gas flow. In general, $N \sim C_\infty D$, where D is coefficient of diffusion; C_∞ is concentration of oxidizer far away from surface of particle (for diffusion in gas,

$D \sim 1/p$; $C_\infty \sim p$ and accordingly $N \neq f(p)$. Then for burning rate we will obtain:*

$$m \sim \frac{1}{d} \sqrt{DC_\infty}. \quad (84)$$

We will examine several special cases.

1. Molecules of oxidizer (for example, KClO_4), which are not decomposed diffuse through the layer of condensed residue (for example, KCl). Here $C_\infty \neq f(p)$ and $D \neq f(p)$. Hence

$$m \sim 1/d \neq f(p) \quad \text{at any } d. \quad (85)$$

2. Molecules of oxidizer are decomposed, yielding oxygen, which diffuses through the layer of liquid residue in the form of bubbles and in dissolved form. In the latter case $C_\infty \sim p$ (according to the law of Henri); coefficient of diffusion D in the first approximation does not depend** on p . Hence

$$m \sim \frac{\sqrt{p}}{d} \quad \text{at any } d. \quad (86)$$

In real conditions, an intermediate case can take place: at sufficiently small d , when surface of components is very great, oxidizer succeeds in diffusing to surface of particles of fuel*** which has still not been decomposed, i.e., case 1 takes place and $m \neq f(p)$. However, at large d , when layers of oxidizer are great, an overwhelming majority of molecules of oxidizer are at first decomposed, and then oxygen diffuses to surface of particles of fuel. If case 2 takes place, then for big particles $m \sim \sqrt{p}$.

A similar explanation will agree with the fact that for mixtures of KClO_4 with big tungsten, dependence $u(p)$ weakens with decrease of KClO_4 content

*We examined the case of nonvolatile particles (for which there is observed only diffusion conditions of burning). Accordingly, $r_\phi/r_k \approx 1$ and $L \ll N$, so that $N + L \approx N$ (see (40)).

**Coefficient of diffusion in solutions depends on concentration of solute; however, this dependence is comparatively weak (moreover, with increase of concentration, there is observed not only decrease but also increase in D ; see § 6B).

***The real problem is more complex, since temperature of burning particle is high and between surface of particle and layer of condensed residue, there is a gas film.

[139] (since thickness of layers of liquid residue decreases and, accordingly the role of diffusion through liquid decreases). Furthermore, in the process of fulfilling work [139], it was found that dependence $u(p)$ is strengthened not only with increase of dimension of particles of metal d_M , but also with increase of dimension of particles of oxidizer d_{ok} (at $d_M = \text{const}$). This result is the easiest of all to understand, if one considers that with increase of d_{ok} , path of diffusion of oxygen through condensed remainder is increased.

C. Expression for Burning Rate During Simultaneous Flow of Homogeneous and Heterogeneous Reactions

In division A of this paragraph, we examined the case in which burning takes place at the expense of homogeneous reaction (inasmuch as mixing of components can be completed in zone of heating). Conversely, in division B the case is examined in which burning takes place at the expense of reaction near surface of particles. We will talk conditionally in this case about heterogeneous reaction.

Besides these cases, the case is also possible when there occurs simultaneously homogeneous reaction in mixture of products of gasification and heterogeneous reaction to particles (see [174]). Particles either can be introduced into the system specially (catalytic or power additions), or can be spontaneously formed in the course of burning (for example, soot).

Let us assume that burning rate of a system not containing particles in the zone of reaction is equal to u , and the burning rate of the system with addition of particles is equal to u' . We will designate their ratio as $u'/u = Z$.

If burning of the system without particles goes on in conditions close to kinetic, then burning rate is proportional to square root of speed of liberation of heat per unit of volume ϕ_{royn} at the expense of homogeneous reaction (see [26, 27]):

$$u \sim \sqrt{\phi_{\text{royn}}} \sim \sqrt{p^{2v} e^{-E/RT_r}}, \quad (87)$$

where p is pressure; v is the exponent in formula $u = bp^v$; E is activation energy; T_r is combustion temperature of system without particles.

With the introduction of additional particles, there appears heat emission at the expense of heterogeneous reaction on surface (or near surface) of particles. In the case in which homogeneous and heterogeneous reaction take place in the same zone, it is possible to write:

$$u' \sim \sqrt{\phi'_{\text{royn}} + \phi_{\text{re1}}} \sim \sqrt{p^{2v} e^{-E/RT_r} + \phi_{\text{re1}}}. \quad (88)$$

where T_p' is combustion temperature in the presence of particles.

We will examine the case in which heterogeneous reaction takes place in diffusion conditions (i.e., its speed is limited by speed of feed of reagents to surface of particles). In this case

$$\Phi_{\text{het}} \sim (\rho_p D / d^2) (u' / x), \quad (89)$$

where ρ_p is density of gas; D is coefficient of diffusion; d is dimension of particles; x is velocity of particles.

For small particles, x is close to speed of gas $v \sim \rho u' / \rho_p$ (where ρ is density of initial system). In this case

$$\Phi_{\text{het}} \sim p / d^2. \quad (90)$$

Putting (90) into (88), we will obtain for value $Z = u' / u$:

$$Z \sim \sqrt{\frac{\frac{E}{R} \left(\frac{1}{T_p'} - \frac{1}{T_r} \right)}{e^{\frac{A'}{RT_p'}} + p^{1-\nu} \frac{A'}{d^2} e^{E'RT_p'}}}. \quad (91)$$

If T_p' does not depend on pressure (i.e., if completeness of burning of particles or expenditure of heat on their heating is constant), then from (91) we will obtain the following dependence:

$$Z \sim \sqrt{A + B p^{1-\nu}}. \quad (92)$$

Consequently, if for the system without particles, index $\nu < 0.5$, then value Z should increase with pressure, but if $\nu > 0.5$, then value Z should decrease with pressure.

From (91) one may also see that Z increases with decrease of dimension of particles d , with increase of T_p' and with decrease of T_p . The latter means that, other things being equal, it is easier to increase the burning rate of a "cold" mixture (i.e., a mixture with a low combustion temperature).

In literature there are certain experimental data, which permit estimating the validity of formula (92). In work [138] there is investigated change of burning rate of stoichiometrical mixture KCIO_4 + bitumen ($\nu \approx 0.73$ in interval 5-100 atm) during addition of particles of tungsten and others. In all cases value Z fell with rise in pressure, which is in accordance with formula (92).

In work [201] the action is studied of addition of particles of charcoal on the burning of PETN ($\nu \approx 0.95$). And in this case, value Z drops with rise in p (accordingly, for PETN with charcoal, index ν decreases to $\nu' = 0.6-0.65$).

S. A. Tsyganov (see [174]) has shown that for gelated mixture of NH_4ClO_4 (~5 microns) + plexiglas, $\alpha = 0.6$, for which dependence $u(p)$ is very weak:

p , atm	25	40	70	100
u , mm/s	9,3	9,3	8,0	8,3

($v_{25-100\text{ mm}} \approx 0$, $v_{10-100\text{ mm}} < 0$). addition of charcoal or Cu_2O strengthens dependence $u(p)$. Accordingly, value Z quickly rises with increase in pressure:

p , atm	Z		p , atm	Z	
	2% soot	2% Cu_2O		2% soot	2% Cu_2O
25	1,04	1,26	70	1,45	2,25
40	1,19	1,59	100	—	2,65

Increase of index v with addition of soot was observed in work [141] for NH_4ClO_4 — paraformaldehyde mixture in that region of pressures where $v = 0$ for the initial system.

Thus, dependence (92) will agree with experimental data available in literature.

D. Theoretical Works on Propagation of Flame Along Surface of Contact of Fuel and Oxidizer

Propagation of flame along flat and cylindrical surface of contact of fuel and oxidizer was investigated experimentally [124, 127, 166], and then theoretically [142-145] as the maximum case of burning of mixture system at a very large dimension of particles of components. However, burning of usual disordered mixtures does not lead only to propagation of flame along surface of contact of components, but also includes the process of transmission of burning from one particle of oxidizer to another through a layer of fuel at the expense of heat addition from neighboring sections of the system [124].

Experimental work on propagation of flame along surface of contact of components will be examined below (§ 18). Here we will very briefly expound on conclusions of theoretical works.

In work [142] the Zel'dovich-Swabian method is used to examine two-dimensional problem about burning of flat layers of fuel and oxidizer on the assumption that masses of oxidizer and fuel are in stoichiometrical ratio that surface of charge turned to flame is flat, etc. The solution is extremely awkward; it is not possible to obtain in evident form an expression for burning rate; neither are results of numerical computations given.

It is indicated that burning rate u practically does not depend on pressure. In § 18 we will see that this result contradicts experiment in almost all cases

investigated.* In an analogous setting the problem of propagation of flame along surface of contact of components was solved in work [143]. Results of the solution are also analogous (in work [143] it was obtained that for diffusion conditions $u \sim 1/h \neq f(p)$, where $2h$ is width of layer, identical for layer of fuel and layer of oxidizer). The method of solution accepted in this work differs from the method accepted in work [142].

In work [145] burning in an ordered system is examined on the basis of ideas of the "two-temperature theory" (on surface of charge there are flat cavities and protuberances where the first correspond to that component which is more easily gasified, and the second corresponds to that component which is more difficult to gasify). The expression for burning rate is not given in evident form numerical calculation is carried out for NH_4ClO_4 - polystyrene and NH_4ClO_4 - polyurethane systems (data are used on speed of pyrolysis on heated plate).

Results are given graphically at coordinates $\lg u$, $\lg d$. For NH_4ClO_4 - polystyrene system at oxidizer-fuel ratio of 90:10 and 80:20, calculation gives direct lines corresponding to dependence $u \sim d^{-n}$, where $n \approx 0.9$ at any d . This result clearly contradicts experiment. Real dependence $u(d)$ is, as a rule, weaker, and, moreover, the slope of curve $u(d)$ (and, consequently, the value of derivative $\partial \ln u / \partial \ln d$) changes with change in d . For NH_4ClO_4 + polyurethane system (at oxidizer-fuel ratio of 90:10 and 80:20) slope of analytic curve (in coordinates $\lg u$, $\lg d$) is strengthened with rise in d , i.e., dependence $u(d)$ is strengthened with increase in d . This result also causes definite doubts. Average (in represented interval d) value of index n in calculated dependence $u \sim d^{-n}$ for NH_4ClO_4 - polyurethane systems is 0.5-0.6, i.e., calculation of dependence $u(d)$ is too strong in this case.

Another approach to solution of examined problem is used in work [144]. This work is as yet the only one which considered the experimental fact that along surface of contact of components there will be formed a wedge shaped cut, in which flame is located. The expression for speed of flame in [144] is found from the condition that on "spout" of flame (i.e., at point of flame closest to fresh substance) critical flow of substance is attained, which chemical reaction can still process in diffusion flame. Expression for burning rate is obtained in evident form. Although it is awkward, it is clear that burning rate should depend on pressure. This also agrees with experiment.

Work [144] also gives an appraisal of absolute value of burning rate. In order of value this appraisal coincides with experimental data of work [124]. Agreement with experiment could be more complete, if in work [144] it was considered that thermophysical properties (especially heat of gasification) of fuel and oxidizer are usually quite different from one another. Therefore, real cut in layer of fuel is sharper than in layer of oxidizer (whereas

*Only for one system (KMnO_4 - plexiglass) (see [127]) in wide range of pressures (5-100 atm) does flame propagation velocity not depend on pressure.

in work [144] symmetric configuration is examined). Appraisal in work [144] of width d_* of layer of component starting with which burning rate ceases to depend on d (computed value of $d_* \approx 0.026$ cm) can pertain to fuel, but not to oxidizer (where experiment gives $d_* \approx 1$ cm). Moreover, d_* depends on pressure (see below).

E. Increase of Burning Rate During Introduction of Inert Addition

It is useful to pay attention to the circumstance that mass (and even linear) burning rate of condensed system, in principle, can be increased with introduction of inert addition [134].

According to (8), mass burning rate $m \sim \sqrt{\frac{2k_p T_{\max}}{q}} \cdot \frac{W_{\max}}{T_{\max}}$. It follows from

this that, other things being equal, m increases with decrease of heat of burning q . The meaning of this result is trivial if q changes especially at the expense of introduction of inert addition.

Index a (active) will denote values pertaining to undiluted system; index i (inert) will denote values pertaining to inert addition. Values pertaining to mixture (active substance + inert addition) will be left without indices. Heat of burning of system with addition $q = q_a (1 - \chi)$, where χ is part by weight of addition. Speed of liberation of heat per unit of volume of flow

$$\phi_{\max} = q_a (\text{cal/g active}) \cdot W_{\max} (\text{g active/cm}^3 \cdot \text{s}),$$

where $W_{\max}$ is mass velocity of reaction of active substance in a mixture containing inert addition (at $T = T_p$). Disregarding changes λ and E , we will obtain:

$$\frac{m}{m_a} \sim \frac{1}{1-\chi} \cdot \frac{T_{\max}}{(T_{\max})_a} \cdot \sqrt{\frac{W_{\max}}{(W_{\max})_a}} \sim \frac{1}{1-\chi} \left[\frac{T_{\max}}{(T_{\max})_a} \right]^{1-n/2} \times \\ \times (1-V')^{n/2} e^{\frac{E/2R}{(T_{\max})_a} - \frac{1}{T_{\max}}}. \quad (93)$$

If one limits himself to the case of sufficiently small particles, then V' (part of volume occupied by particles in two-phase flow) is minute (i.e., $1 - V' \approx 1$). In formula (93) at growth χ factor $1/(1 - \chi)$ influences in the direction of increase of m/m_a at that time that very fast lowering of

$W_{\max}/(W_{\max})_a$ (due to lowering of $T_{\max}/(T_{\max})_a$) influences in the direction of decrease of m/m_a . Resultant value m/m_a in case of introduction of inert addition can be both less and more than one, but not more than $1/(1 - \chi)$ (the maximum value of m/m_a is 1.11 at $\chi = 0.1$; 1.25 at $\chi = 0.2$, etc.).

The meaning of factor $1/(1 - \chi)$ in formula (93) becomes clear if m is depicted in the form of sum of flow of active substance $m(1 - \chi)$ and inert

addition $m\chi$. Then for mass burning rate of active substance, we will obtain

$$(1-\chi)m \sim \sqrt{\frac{1}{q_a} \lambda W_{\max} \frac{RT_{\max}^2}{E}},$$

i.e., mass burning rate of active substance can only decrease with increase in χ .

Thus, member $1/(1-\chi)$ describes increase of mass burning rate at the expense of admixing of mass of inert substance. For addition of inert particles with small heat capacity and high density, it is possible to approach sufficiently near to the limiting value $\frac{m}{m_a} \sim \frac{1}{1-\chi}$. Regarding burning rate, using relationships analogous to those given in § 7B, it is simple to obtain expression:

$$\frac{u}{u_a} = \frac{m}{m_a} \frac{\rho_a}{\rho} \left(1 + \frac{\chi}{1-\chi} \frac{\rho_a}{\rho_{\text{inert}}}\right) (1-V'')^{n_2} \left[\frac{T_{\max}}{(T_{\max})_a}\right]^{1-n_2} \times e^{\frac{k}{2H} \left[\frac{1}{(T_{\max})_a} - \frac{1}{T_{\max}}\right]}. \quad (94)$$

In this expression factor $1 + \frac{\chi}{1-\chi} \frac{\rho_a}{\rho_{\text{inert}}}$, increasing together with χ , gives the limit of increase of u/u_a . Presence of this factor is connected with the fact that at identical speed of reaction in gas phase, burning rate of system with inert addition should be higher, in order to succeed in passing necessary quantity of substance into zone of reaction (small inert particles occupy noticeable part of volume in solid phase and a negligible part in two-phase flow).

§ 9. Multidimensional Burning Behavior of Condensed Mixtures

For sufficiently finely dispersed ($d \leq d_{\min}$) mixtures with gasified components, burning takes place in kinetic conditions, and front of burning is flat (Fig. 18a). When d becomes larger than $d_{\min}$, cones of mixing cease to find a place within limits of zone of heating. On surface of front, there appear coneshaped protuberances where burning already has a diffusion character (Fig. 18b). Dimensions of protuberances increase with increase in d , and surface of front is more and more distorted (Fig. 18c).

It is essentially, however, to note that at any arbitrarily large d , "spouts" of flame are in homogeneous mixture, since mixing of components starts earlier than reaction between them. Accordingly, burning in "spouts" (in a zone on the order of $d_{\min}$ wide) proceeds in kinetic conditions, but above there is disposed a diffusion flame (on the order of md^2/D high).

Regarding surface of condensed phase, it, in general, is not flat even at $d < d_{\min}$ (due to difference in speed of gasification of components). At large d along surfaces of contact of components, there will be formed deep cuts inside which burning occurs.

Thus, at $d > d_{\min}$ burning of condensed mixtures is essentially multidimensional. Front of burning consists of totality of tongues of flame, "spouts" of which deeply delve into condensed phase along surfaces of contact of components. In their upper part, tongues of flame merge into a single diffusion flame.

Multidimensionality of surface of condensed phase can be distinctly observed with the help of filming in the burning process (Fig. 19), and also during



Fig. 19. Burning of spherical particles of NH_4ClO_4 in a block of polymethylmethacrylate [232].

**GRAPHIC NOT
REPRODUCIBLE**

examining of liquidated charges. Moreover, in some conditions, crystals of oxidizer will form protuberances, and layer of fuel cavity; in other conditions — conversely. Observation of a burning surface is not infrequently complicated by the fact that gasification of every given crystal of oxidizer or layer of fuel passes unsteadily. Furthermore, on the surface there is not infrequently liquid or solid condensed remainder. During the study of extinguished charges, there are possible errors combined with delay in extinguishing (the time during which it is possible to suppress the process of gasification can be different for fuel and oxidizer).

In a number of experimental works [105, 146, 147, 217], it is noted that at high pressures and high burning rates, NH_4ClO_4 crystals form on surface of cavity, but layer of fuel forms on surface of protuberance. At low pressures and low burning rates, this difference is smoothed or crystals of oxidizer start to form protuberances. As a fuel in work [105], there was used thiocol; in work [146] there was used 2.4 parts by weight unsaturated polyester and 1 part by weight nitroglycerine.

In work [217] this structure of surface of charges was observed for mixtures of NH_4ClO_4 with malonic and amber acids and starch. For a mixture of NH_4ClO_4 with naphthalene (very volatile fuel) on surface of liquidated charges, there was only NH_4ClO_4 (and a certain quantity of products of decomposition of naphthalene). Conversely, for a mixture of NH_4ClO_4 with tungsten, on surface there was stored tungsten (nonvolatile component).

In § 6C we already mentioned results of work [124], in which there was measured form of cut forming in plate of plexiglas during burning in system; a layer of KClO_4 of thickness d between two thick plates of plexiglas. Experiments were conducted at 1 [atm(abs.)] in nitrogen, where at a definite tune, the flame was sharply extinguished by a stream of water. Relief of plates was measured on a microscope with micrometric supply along three mutually perpendicular axes. Figure 20 shows the average profile of cut by many measurements for

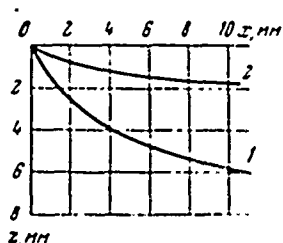


Fig. 20. Average profile of cut, forming in plate of plexiglas during burning in contact with KClO_4 ($\delta = 0.68$) at

1 [atm(abs.)] [124]. x is distance along length of plate; z is depth of burning out, origin of coordinates in "spout" of flame. 1 — $d_{\text{KClO}_4} = 25$ mm; $u = 0.50$ mm/s; 2 — $d_{\text{KClO}_4} = 3.8$ mm; $u = 0.98$ mm/s.

25 and 3.8 mm thick layer of oxidizer. Angle of burning out ϕ (i.e., angle between tangent to profile of cut and direction of propagation of flame) smoothly decrease with distance from spout. On initial section (2-3 mm), mean value of ϕ is $\sim 32^\circ$ for $d = 25$ mm and $\sim 13^\circ$ for $d = 3.8$ mm. Let us note that burning rate increased with decrease in d (from 0.50 mm/s at $d = 25$ mm to 0.97 mm/s at $d = 3.8$ mm). Thus, angle of burning out becomes sharper with increase in burning rate at the expense of decrease in d .

Angle of burning out also becomes sharper in the case when burning rate is increased at the expense of increase in pressure. In that same work [124], there was measured average angle of burning out (measured on thickness $d = 0.9$ mm) for vinyl plastic:

P , atm	10	20	30	40
u , mm/s	1.37	2.12	2.43	2.73
ϕ_{cp}	19°	14°50'	14°40'	13°

These data can be described by empirical formula $\sin \phi \approx 0.4 u^{-0.55}$.

Reliable measurement of angle of burning out in layer of oxidizer in work [124] did not prove feasible since surface of layer of oxidizer was damaged during extinguishing by water. Measurements in the course of burning (in the case of such oxidizers as KClO_4 , KClO_3 , KMnO_4 and BaO_2) are hampered

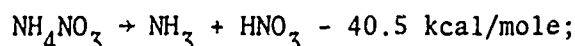
by the presence of condensed residue. Tentative measurements (on appearance of colors of iridescence on needles introduced into layer of oxidizer) gave for KClO_4 (at 1 [atm(abs.)] and $d = 25$ mm) $\phi \approx 55-65^\circ$.

§ 10. Multistageness of Burning of Condensed Mixtures

In case of mixture systems with gasified components (at $d > d_{\min}$, there are two zones of burning: in points of flame most advanced in the direction of fresh mixture, burning goes on in kinetic conditions, but above there is disposed a diffusion flame.

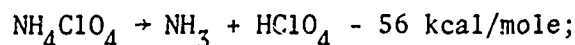
In works [97, 104, 118] and others it is assumed that for systems on the basis of NH_4NO_3 and NH_4ClO_4 there exists also a third zone, where an exothermic reaction takes place. In this zone, located directly above surface of crystal of oxidizer, there occurs burning of products of its gasification.

In case of NH_4NO_3 , oxidizer is gasified according to diagram:



ammonia and nitric acid vapor form near surface of crystal flame with design temperature $\sim 1250^\circ\text{K}$ [97, 118].

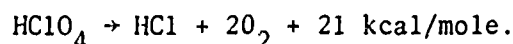
In case of NH_4ClO_4 , oxidizer is gasified according to diagram:



ammonia and chloric acid vapor burn near surface of crystal (design temperature of flame is 1380°K at 1 [atm(abs.)] [150]).

It would be of interest to study characteristic of flame of $\text{NH}_3 + \text{HClO}_4$ directly, but this is hindered by methodical difficulties. However, it was possible to study burning of pure HClO_4 (flame of disintegration) and burning of HClO_4 mixtures with H_2 , CH_4 , CO and others [148, 149].

Disintegration of HClO_4 at high temperatures proceeds according to diagram [148]:



In work [148] there is studied burning of vapors of 72% aqueous solution of HClO_4 (this corresponds to relationship $\text{HClO}_4 + 2.17 \text{ H}_2\text{O}$)* at 210°C . There is obtained value $u_H \approx 19 \text{ cm/s}$, $m \approx 0.021 \text{ g/cm}^2\cdot\text{s}$, design temperature of flame is 1076°K .

*Anhydrous HClO_4 is too unstable.

During addition of gaseous fuel to HClO_4 vapors, speed and combustion temperature essentially increase (Table 33).

Table 33. Mass Speed and Combustion Temperature of Homogeneous Mixture ($\text{HClO}_4 + 2.17 \text{H}_2\text{O} + x \text{N}_2$) - Gaseous Fuel [149], $p = 1$ [atm(abs.)], $T_0 = 210^\circ\text{C}$

Fuel	x	$m, \text{g/cm}^2 \cdot \text{s}$				x_{max}	$x_{f_{\text{max}}}$	$T_{\text{max}}, ^\circ\text{K}$	$T_{\text{z}}, ^\circ\text{K}$
		$x = 1$	$x = 0.95$	$x = 0.9$	$x = 0.8$				
CH_4	1	0.48	0.558	0.46	0.41	0.67	0.40	2620	2620
CO	0	0.285	0.334	0.388	0.37	0.50	—	—	—
CH_3OH	2	0.459	0.503	0.395	—	0.72	0.41	2520	2505
C_2H_6	1	0.502	0.545	0.482	—	0.72	0.84	2650	2640

At equal combustion temperature, burning rate of mixtures with HClO_4 is higher than with oxygen [149]. Consequently, HClO_4 does not simply disintegrate with yield of O_2 , but is itself a more active oxidizer. Mass burning rate of pure NH_4ClO_4 at 1 [atm(abs.)] and $200\text{--}220^\circ\text{C}$ is $0.029\text{--}0.036 \text{g/cm}^2 \cdot \text{s}$ [47], i.e., considerably less than value m for mixtures of HClO_4 with gaseous fuels. This is natural since gasification $\text{NH}_4\text{ClO}_4 \rightarrow \text{NH}_3 + \text{HClO}_4$ is a strongly endothermic process, and combustion temperature of NH_4ClO_4 is low (1380°K).

Mass rate of NH_4ClO_4 - polyester compounds [151] at 1 [atm(abs.)] and 200°C lies within limits of $0.20\text{--}0.27 \text{g/cm}^2 \cdot \text{s}$, i.e., already close enough to values of m for mixtures of HClO_4 with gaseous fuels (but still below them).

Direct observations of examined kinetic zones of burning are very hampered since distance from these zones to surface of charge (calculation) can be $10^{-3}\text{--}10^{-5} \text{cm}$. Only during burning of comparatively big (several millimeters) balls of NH_4ClO_4 in propane [232] are there well noticeable on photograph two zones of burning, of which the one directly adjoining the surface of the ball, apparently, corresponds to burning of $\text{NH}_3 + \text{HClO}_4$.

A. Leading Stage of Burning

In Chapter I we noted that for homogeneous condensed explosives and even homogeneous gas systems, burning can proceed in several spatially divided stages. This is connected with peculiarities of kinetics of chemical reactions in such flames (transformation is accomplished in steps). Let us note that such "chemical multistageness," of course, can also take place for mixture systems. However, existence of several zones of burning examined at the beginning

of this paragraph is connected, not with "chemical multistageness," but with the presence in a system of two different components (one of which, the oxidizer, is capable of independent burning) and multidimensionality of burning.

The central question of multistage burning is the question of how much every stage affects burning rate (in other words, how much burning rate would be changed if one were to accelerate or decelerate reaction at a given stage, not changing speed of reaction on remaining stages).

In § 5 we already examined this question for homogeneous systems. For homogeneous systems in a number of works (for example, [138, 153] and others), the assumption is expressed that during multistage burning, there is not infrequently one leading stage which determines burning rate. Other subordinated stages are constructed under this speed.

This assumption is convincing for the case of a plane front of burning (which was only examined in the above mentioned works). Actually, for flat front of burning at rated temperature and composition of reagents, there is only one value of burning rate [154]. If one introduces catalytical addition, which, for example, increases speed of transformation of parent substance into half-finished products, changing neither their temperature nor their composition, then zone of leading reaction will start to contact increasing flow of half-finished products in the direction from surface of charge until as a result of decrease of heat flow from leading stage, speed of subordinated stage again returns to its initial value. Only profile of temperatures throughout zones of burning will be changes, in particular, temperature on surface of charge will decrease.

Considerations given here pertain to the case in which leading stage is located further from fresh substance than subordinated stages. In the opposite case, when subordinated stages are located further from fresh substance than leading stage during accidental increase of speed of leading stage (and constant speed of reaction in subordinates stage), one would think that zone of subordinated reaction should be brought down by flow (i.e., such a configuration would be unstable). In fact, this does not happen (see § 5).

The question about the existence of leading stage during burning of condensed mixtures was examined in work [155].

During transition to multidimensional burning characteristic for condensed mixtures* at $d > d_{\min}$ (see above), those logical considerations from which there came the necessity of the existence of leading stage of burning lose their force.

Indeed, for multidimensional burning to rated temperature and composition of reagents, there no longer corresponds only value of burning rate, since there is one more independent parameter — surface of front of burning per

*Multidimensional burning can also take place for homogeneous systems if it is accompanied by formation of condensed residue (for example, flakes of soot).

unit of cross section of flow.

As an example we will examine the case which is usual enough for condensed mixtures when oxidizer is capable of independent burning, but fuel is gasified under the influence of heat flow from without. Half-finished products formed during burning of oxidizer are mixed with half-finished products formed during gasification of fuel, and they form a flame, which near "spout" is a kinetic flame, and higher up is a diffusion flame.

We will introduce a catalytic addition, which, for example, accelerates burning of oxidizer (changing neither temperature nor composition of half-finished products). This should immediately change form of surface of charge and form of diffusion flame. Let us assume that, for example, initially gasification of fuel and oxidizer was completed in the same plane. After introduction of addition, which activates decomposition of oxidizer but does not affect gasification of fuel, particles of oxidizer will form cavities and particles of fuel will form protuberances. Accordingly, form of diffusion flame will be changed. And burning rate will be changed since there is no condition in which it would remain constant during two different configurations of the zone of burning.

Regarding diffusion flame, it is also not a subordinated stage. Direct experiments (see § 13) show that, changing speed of diffusion flame at the expense of change of dispersiveness of components, we change burning rate on the whole.

Thus, according to theoretical concepts speed of multidimensional multistage burning is not determined by processes going on in any one stage.

However, the influence of different zones on burning rate, of course, is not the same. For condensed mixtures the proposition remains in force, according to which burning rate is essentially influenced only by zones which are not too distant. In division B of this paragraph, we will examine this question in greater detail. It is necessary, however, to consider that the influence of a given i -th stage on burning rate cannot be correctly estimated if one considers only direct heat transfer from this zone to fresh substance. Of greater essence can appear additional flows of heat from all $i - 1$ stages (between fresh substance and i -th stage), connected with increase of temperature within limits of these zones due to heat addition from the i -th stage. Therefore only that zone is "sufficiently distant" which is located far not only from fresh mixture, but also from intermediate zones of burning.

Direct observation of all zones of burning examined above of mixture systems involves great experimental difficulties and as yet has not been carried out. All the more so, it has not been possible up to now to clarify by direct experiments how much burning rate is affected by each of these zones. In literature there are only indirect considerations on this matter.

In works [97, 113, 118] it is assumed that for mixtures on the basis of NH_4NO_3 , a basic role is played by $\text{NH}_3 + \text{HNO}_3$ flame near surface of crystals of oxidizer. In favor of this assumption, the following arguments are given:

- 1) many powders and model mixtures on the basis of NH_4NO_3 have the same

burning rate as NH_4NO_3 without fuel (both NH_4NO_3 and compounds based on it, contain the same catalytical addition);

2) change of molecular weight of polymer strongly affects speed of pyrolysis and, therefore, should strongly affect characteristics of diffusion flame.* Meanwhile burning rate practically does not change during change of molecular weight of polymer.

Regarding compounds based on NH_4ClO_4 , in works [104, 141] and others, it is assumed that in this case, too, a basic role is played by the flame of products of decomposition of oxidizer ($\text{NH}_3 + \text{HClO}_4$). Moreover in work [141] it is fundamentally indicated that it is necessary to consider increase of temperature in zone of $\text{NH}_3 + \text{HClO}_4$ flame as a result of heat addition from diffusion flame (this leads to increase of burning rate).

In work [104] an appraisal is given of distance Δ between surface of crystal NH_4ClO_4 and flame $\text{NH}_3 + \text{HClO}_4$. This distance is very small (on the order of one micron).

Such an appraisal is easy to obtain from the equation of heat balance on the assumption that burning rate is determined only by zone of flame $\text{NH}_3 + \text{HClO}_4$:

$$\rho u [c(T_u - T_0) + Q] = \lambda \left. \frac{dT}{dx} \right|_n \approx \lambda \frac{T_r - T_u}{\Delta}, \quad (95)$$

where for NH_4ClO_4 $\rho = 1.95 \text{ g/cm}^3$; $c = 0.26 \text{ cal/g} \cdot \text{deg}$, heat of gasification $Q = 56 \text{ kcal/mole} = 477 \text{ cal/g}$. Let us take also $\lambda \approx 2 \cdot 10^{-4} \text{ cal/cm} \cdot \text{s} \cdot \text{deg}$, $T_r = 1110^\circ\text{C}$.

At 35 atm ($T_n \approx 680^\circ\text{C}$ [130], $u \approx 0.3 \text{ cm/s}$) we will obtain from (95) value $\Delta \approx 2.3 \text{ microns}$, but at 70 atm ($T_n \approx 720^\circ\text{C}$ [130], and $u \approx 0.7 \text{ cm/s}$) value $\Delta \approx 0.9 \text{ microns}$.

Although experimental dependences of speed of multistage burning on pressure, initial temperature, etc., hardly differ from analogous dependences for monophasic burning, a theoretical expression for speed of multistage burning has not yet been obtained (see § 5). It is true that in literature sufficiently wide propagation has been obtained by the formula of Summerfield [105] for dependence of speed of diphasic burning (kinetic zone + diffusion zone) on pressure:

$$\frac{1}{u} = \frac{a}{p} + \frac{b}{\sqrt{p}}, \quad (96)$$

*Such a conclusion is not obvious by a long shot, especially as it has not been checked by experiment.

a is determined by kinetic factors (in particular, $a \sim e^{E_{\text{act}}/RT}$). Coefficient b is determined by diffusion factors (in particular, $b \sim d$). However, during combustion (96), there was made a number of arbitrary assumptions,* and, therefore, it should be considered only as an empirical formula (useful for those mixtures for which index ν in formula $u = bp^\nu$ is larger than 1/3).

B. Zone Affecting Burning Rate

Of great use for explanation of experimental data were ideas (formulated in works [124, 156] and others) about the fact that burning rate of mixture systems is influenced by not the whole zone of transformation of initial mixture into end products of combustion, but by only a certain part of this zone ("zone of influence," "active zone of burning," etc.) adjoining surface of charge.

Certain ideas about width of zone of influence can be obtained from experiments [124] for propagation of flame along surface of contact of flat layers of plexiglas and KClO_4 . On surface of plate of plexiglas different thin films were pressed or deposited from solution. For films of polyethylene, with increase of their thickness Δ , speed of flame at first increased and then (Fig. 21)

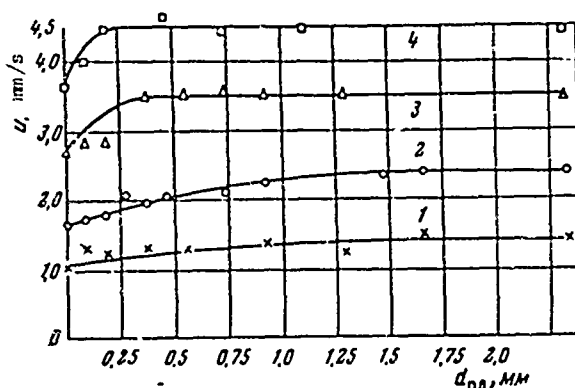


Fig. 21. Speed of flame in system layer KClO_4 ($\delta = 0.68$) + layer of polyethylene of different thickness d_{nn} + thick foundation of plexiglas [124] at different pressures: 1 - 5 [atm(gage)]; 2 - 10 [atm(gage)]; 3 - 20 [atm(gage)]; 4 - 30 [atm(gage)].

at a certain thickness Δ_* , it reached a plateau. Value Δ_* , apparently, is equal to thickness of layer of film capable of burning in zone of influence.

*It is accepted that products of gasification of fuel and oxidizer will form separate "packs," where mass "of pack" does not depend on pressure and is small as compared to mass of crystal of oxidizer of layer of fuel. It is also accepted that temperature gradient can be recorded in the form $(T_r - T)/(\ell_k + \ell)$, where ℓ_k and ℓ are widths of kinetic and diffusion zone, etc.

further (above Δ_*) increase of thickness of layer of polyethylene no longer affects burning rate since the latter "does not know" what is going on outside the zone of influence — whether polyethylene or plexiglas is burning there. With increase of pressure, value Δ_* decreases (from $\Delta_* \approx 0.9$ mm at 10 [atm(gage)] to $\Delta_* \approx 0.2$ mm at 30 [atm(gage)]). If angle of burning out of polyethylene is equal to ϕ , then height of zone of influence is equal to $h_{\text{вп}} \approx \Delta_* \text{ctg } \phi$. Angle of burning out was not measured for polyethylene. If one allows that value ϕ for polyethylene is the same as for vinyl plastic, then for $h_{\text{вп}}$ we will obtain at 10 atm $h_{\text{вп}} \sim 0.9 \text{ctg } 19' \approx 2.6$ mm, and at 30 atm $h_{\text{вп}} \sim 0.2 \text{ctg } 11'40' \approx 0.76$ mm.

Furthermore, dimension of zone of influence for ordered systems can be estimated, proceeding from dependence of speed of flame u on thickness of layer of oxidizer $d_{\text{ок}}$. With increase in $d_{\text{ок}}$ speed of flame at first drops, and then at a certain $(d_{\text{ок}})_*$ reaches a plateau (Fig. 54). Thus as in case $*$, value $(d_{\text{ок}})_*$ is equal to thickness of layer which can burn in zone of influence. For KClO_4 — plexiglas system value $(d_{\text{ок}})_* \approx 5\text{--}6$ mm [124, 127].

is not possible to calculate height of zone of influence, proceeding from since angle of burning out in layer of oxidizer was not measured.

In usual disordered mixtures, dimension of zone of influence and part of components which react in zone of influence should depend on dimension of particles of components, and also on pressure, etc. Special experiments, in which zone width of influence would be measured, have not yet been conducted.

However, based on experimental dependences of burning rate on dispersiveness of components, ratio of components, pressure, etc., (see Chapter III), a number of conclusions can be reached. For ordinary, disordered mixtures, dimensions of zone of influence, apparently, are significantly less than for the ordered systems which we just examined. Already at dimension of particles of oxidizer in several hundreds of microns (and not too low pressures) components do not completely react in zone of influence. The fraction of components reacting in zone of influence quickly drops with increase in d (however, absolute dimension of zone of influence, apparently, somewhat rises with increase in d).

Heat expended on heating of particles which react far from zone of influence, in general, is not compensated by supply of heat from distant sections of flame. Consequently, the presence of such particles in zone of influence leads only to losses of heat. In other words, burning in zone of influence goes on in the presence not only of sources of heat (at the expense of chemical reaction), but also of escapes of heat (at the expense of heat withdrawal in particles reacting outside zone of influence). Other things being equal, thermal losses are higher the larger the temperature transfer of particles and the smaller the particles.

In many cases, components at first gasify and only then react among themselves. If dimension of particles of components is sufficiently small and their volatility is high, particles are gasified completely and relationship between components is the same as in initial mixture. However, with increase in dimension of

les of components within limits of zone of influence, there gasify in different fractions of fuel and oxidizer. Accordingly, ratio of components in gas phase starts to differ from ratio of components in initial mixture in the direction of surplus of the more volatile component.*

As we noted that during burning of usual disordered mixtures, speed of gasification of components depends on heat of gasification. From this point of view, for mixtures which are not too finely dispersed, the gas phase within limits of zone of influence, apparently, contains more oxidizer than the initial mixture since heat of gasification of KClO_4 is close to zero, and decomposition of NH_4ClO_4 and NH_4NO_3 is accompanied by formation of $\text{NH}_3 + \text{HClO}_4$ (or $\text{NH}_3 + \text{HNO}_3$) flame and goes on with liberation of heat. Regarding usual organic fuels, their gasification requires considerable expenditure of heat.

C. Model: "Burning of Particle of Oxidizer + Gasification of Layer of Fuel"

As we already noted, in a number of works [104, 141] and others, it is assumed that burning rate of compositions based on NH_4ClO_4 is equal to burning rate of crystals of pure NH_4ClO_4 , taking into account increase of temperature in zone of $\text{NH}_3 + \text{HClO}_4$ flame at the expense of heat addition from diffusion flame.

However, it is necessary to consider also speed of transmission of burning from one crystal of oxidizer to another through a layer of fuel. In this connection it is of some interest to give an account of the following elementary model of burning. Let us assume that crystals of oxidizer, identical in dimension, are evenly distributed in fuel. Time of burning of section of charge $d_{ok} + d_f$ long is equal to $d_{ok}/u_{ok} + d_f/w$, where u_{ok} is burning rate of crystal of oxidizer (taking into account supply of heat from flame); w is speed of gasification of layer of fuel at the expense of heat addition from diffusion flame. Average burning rate of composition:

*In this respect, burning of condensed mixtures which are not too finely dispersed is somewhat analogous to diffusion burning of multicomponent combustible liquids (for example, oil) (see [49]) or to burning of liquid explosive mixtures [218]. In these cases, the composition of the vapor phase (in which burning takes place) can also essentially differ from composition of initial mixture in the direction of surplus of volatile component. However, for liquid mixtures, burning is nonstationary: the most volatile components burn first; accordingly, burning rate can continuously change (for liquid explosive mixtures there were also observed periodical fluctuations in burning rate [218]). Conversely, for condensed mixtures, burning can be completely stationary; the part of the components which did not gasify within limits of zone of influence is not mixed with initial mixture, but is carried to zone of diffusion flame where it burns.

$$u = \frac{d_{ok} + d_r}{d_{ok}/u_{ok} + d_r/\sigma} \quad (97)$$

Speeds u_{ok} and w depend differently on pressure. For NH_4ClO_4 at $p \leq 100-125$ atm $u_{ok} \approx bp$. Conversely, w (as can be seen from § 6B) depends on pressure very weakly: $w \approx b'p^{0-0.25}$. Considering in first approximation $w \neq f(p) = b'$ and designating $d_{ok}/d_r = k$, we obtain from (97):

$$u = \frac{k+1}{k/p + 1/b'} = \frac{(k+1)b'p}{b'k + bp} \quad (98)$$

where b , b' and k do not depend on pressure.

From (98) it follows that at pressures which are not too high, u essentially depends on pressure (at $bp \ll b'k u \sim p$). Conversely, at sufficiently high pressures, burning rate practically reaches a plateau* (at $bp \gg b'k u = \text{const} = b'(k+1)$). The meaning of this plateau is obvious: at high pressures, time of burning of crystal of oxidizer is negligible as compared to duration of transmission of burning through layer of fuel (i.e., burning rate of charge is equal to speed of gasification of layers of fuel multiplied by $(k+1)$).

In spite of all the primitiveness of such a diagram, it, apparently, can reflect peculiarity of burning of systems with low volatile bond.

§ 11. Influence of Condensed Residue on Dependence of Burning Rate on Pressure

In certain cases gasification of fuel or oxidizer is accompanied by formation of solid or liquid residue.

In some cases (for example, for mixtures based on KClO_4), on surface of charge there will be formed a layer of residue of definite final thickness (during steady state of burning, speed of formation of condensed residue on surface of fresh substance is equal to speed of removal of condensed residue by gas on external surface of layer). Burning of products of gasification can occur either above layer of residue or inside it (in bubbles and streams),

*Taking for speed of gasification value $w \approx 0.5$ mm/s (see § 6B), and for value $k = d_{ok}/d_r$ value ~ 5 (corresponding to 30% by weight of bond), we obtain value of terminal velocity of burning $u_{\max} \approx 3$ mm/s, which is a reasonable value.

other cases (for example, during burning of KMnO_4 or BaO_2 in shell plexiglas), layer of condensed residue continuously increases with burning. Volume of slag formed can be approximately equal to volume of initial charge or even exceed it). Burning of products of gasification knowingly goes on inside layer of residue.

Obviously, presence of layer of condensed residue can strongly affect mixing of components, heat transfer from zone of burning to fresh substance etc., and this means it can affect dependence of burning rate on different parameters. This question has been investigated very little so far.

In this paragraph we will examine only one possible mechanism of influence of condensed residue on dependence $u(p)$.

Usually burning rate of condensed systems (both heterogeneous, and homogeneous) monotonously increases with rise in pressure, so that index ν in formula $u = bp^\nu$ remains larger than zero.

However, there has been described a large number of systems, for which in the defined interval of pressure $\nu = 0$. It is considerably more rare to encounter a system for which in a certain interval of pressure, $\nu < 0$. Burning of at least part of such systems is accompanied by formation of condensed residue (for example, burning of mixture $3 \text{ Mg} + \text{Cr}_2\text{O}_3$ [157], burning of potassium picrate [70] burning of BaO_2 in a shell of plexiglas [127] and others).

In work [158] it is shown that during certain conditions, presence of condensed residue can by itself lead to $\nu \leq 0$.

Let us assume that transformation of initial system takes place in two stages (we omit their interaction, assuming it to be trivial; we will consider that the second stage is the leading stage and wholly determines the speed of the first stage). On the first stage, the initial system is decomposed with formation of condensed residue (in quantity χ g on 1 g of initial system) half-finished gas products (in quantity $(1 - \chi)$ g on 1 g initial system). The latter react in the second stage.

We will examine the case in which condensed residue forms a dense layer of thickness y_* (through which there break bubbles or streams of gaseous half-finished products), and at $y > y_*$, it is loosened. Accordingly, during transition through $y = y_*$, speed of gas falls.

Let us assume that at a certain pressure, zone of leading reaction is located outside of dense layer. With increase of pressure, this zone will approach fresh substance. However, as soon as it approaches the dense layer (at $p = p'$), increase of speed of reaction in gas phase cannot increase burning rate since zone of reaction cannot penetrate layer of condensed residue (there speed of gas is higher than burning rate). Starting from this moment (and as long as pressure is insufficient for burning to penetrate into layer of condensed residuum), dependence $u(p)$ will be determined by dependence $y_*(p)$.

Meanwhile cases are possible in y_* should grow which with increase of

pressure of thickness of dense layer of residue. Let us consider, for example, the case in which there is a layer of viscous liquid or cohering particles and removal of residue occurs due to breaking of viscous film during yield of bubble of gas to surface. With such conditions, removal of residue is proportional to flow of bubbles Π and square of radius of bubbles. So that thickness of layer of residue is stationary, it should be not too large — such that on length y_* there still occurs essential expansion of bubble. If this condition is carried out, then during accidental decrease in y_* , there decreases radius of bubbles going to surface of layer, and speed of removal of residue becomes less than speed of its formation, so that y_* returns to steady-state value (of course, steady-state operation is possible only for a definite interval, χ).

We will now see how steady-state value y_* will change with change in p . Let us assume that at $p \leq p'$ (p' is the pressure at which zone of reaction "sits" on dense layer of residue) burning rate is proportional to p^v , where $v > 0$. Volumetric flow rate of gas through layer of residue is proportional to p^{v-1} , therefore, at $v < 1$, with rise in pressure Π or volume of bubble in given section should decrease, and y_* should accordingly increase (law of rise in y_* depends on speed of expansion of bubble inside layer). Until $p < p'$, increase in y_* affects neither burning rate nor its dependence on pressure (neglecting change of coefficient of thermal conduction). However, at $p > p'$ increase in y_* should lead to lowering of burning rate. With further increase in pressure there will occur either damping of burning or burning will penetrate inside layer of residue, i.e., transition will occur from one condition of burning to another.

Besides cases of increase of y_* with rise in pressure, a maximum on curve $u(p)$ can be observed in those cases when at low pressures, in general, there will not be formed dense condensed residue and at a certain pressure, p_* the residue "sits" and will form a dense layer. Accordingly, at $p = p_*$ burning rate can start to drop with rise in p .

It would be interesting to trace experimentally change of density and width of layer of condensed residue during change of p for those systems for which in certain interval of pressure, $v < 0$. This problem is complicated by the fact that width of zone affecting burning rate cannot exceed ten microns. Let us note that from the point of view of the ideas examined, systems for which $v < 0$, have to be sensitive to influences affecting thickness and density of condensed residue.

Thus, for example, introducing into the system additions which prevent the formation of an adhering layer or volatile additions which loosen the layer or introducing sufficiently energetic blowoff of surface, it is possible to calculate change of form of curve $u(p)$.

CHAPTER III

DEPENDENCE OF COMBUSTION RATES OF CONDENSED MIXTURES ON VARIOUS PARAMETERS (EXPERIMENTAL DATA)

The number of parameters which affect burning rate of condensed mixtures is greater than for other types of systems:

	Condensed mixtures	Homogeneous gas mixtures	Homogeneous condensed VV
Nature of components	+	+	+
Relationship between fuel and oxidizer ..	+	+	—
Pressure	+	+	+
Initial temperature	+	+	+
Dispersiveness of components	+	—	—
Relative density	+	—	+
Catalytical additions	+	+	+

It is necessary to emphasize that each of the parameters enumerated affects burning rate of condensed mixtures, not separately, but in close contact with each other. Thus, for example, the form of curve $u(p)$ can strongly depend on α , and, in a number of cases, also on d and T_0 . In turn, pressure can affect curve $u(\alpha)$, etc. Below in corresponding divisions, we will examine the most important part of these interconnections.

Considerable part of works on burning of mixture systems pertains to solid fuels (and modelling their compositions) on the basis of NH_4ClO_4 . Therefore, data on burning of pure NH_4ClO_4 (see § 19) and NH_4NO_3 are of definite interest.

*Form of particles (and in certain cases, orientation of particles with respect to front of burning) is also essential.

Let us consider also regularities of propagation of flame in ordered systems consisting of flat or cylindrical layers of components (§ 18). A small division is dedicated to burning of black powder — the oldest mixture system (§ 20).

There, where possible, results of experiments are compared with ideas about burning of condensed mixtures expounded in Chapter II.

§ 12. Types of Condensed Mixtures. Method of Measurement of Speed of Burning

According to their purpose, properties of components, relationship between components, etc., condensed mixtures differ in especially great variety. Accordingly, absolute value of burning rate and dependence of burning rate on different parameters can be strongly changed during transition from one group of mixtures to another.

Depending upon their assignment, condensed mixtures are divided into solid fuel mixtures (for rocket, air-breathing jet, and hydrojet engines for greater detail see books of A. A. Shidlovskiy [159], Ya. M. Paushkin [222], B. V. Orlov and G. Yu. Mazing [223] and others) and pyrotechnic mixtures (igniting, illuminating, igniter, and other compositions [159]).

For the theory of burning of condensed mixtures, which is examined in this work the question about the nature of fuel in a given composition is essential. From this point of view, it is possible to isolate: 1) compositions in which organic fuel is used (capable of being gasified at not too high a temperature), and metal is used only in the form of addition (for improvement of power properties); 2) compositions in which the basic fuel is metal (usually magnesium or aluminum), and organic fuel is used as an addition, which improves mechanical properties of charge.

Regularities of burning of these two groups noticeably differ from each other. During change of relationship between fuel and oxidizer, the maximum burning rate $u_{\max}$ for the first group of mixtures lies near stoichiometry (usually at a small surplus of fuel — at $\alpha = 0.7-0.9$), whereas for the second group of mixtures, $u_{\max}$ frequently will shift distantly in the direction of surplus of fuel (up to $\alpha \leq 0.1$).

Dependence of burning rate on dispersiveness of components is weaker for the first group of mixtures than for the second. Conversely, weak dependence of burning rate on pressure is much more frequently observed for mixtures belonging to the second group.

In the present work, we have examined chiefly the first group of mixtures, since the majority of data available in literature belong namely to such mixtures.

Methods of measurement of burning rate. Existing methods of measurement of burning rate of condensed systems can be divided into three groups, depending upon which physical phenomenon accompanying burning is used in the given method (Table 34). In laboratory conditions the method of burning wires is most

Table 34. Methods of Measurement of Burning Rate

The phenomenon being measured at the base of the given method	Method of measurement	What is measured	Continuity* and spontaneity** of measurement	Influence of transducers on measured process	Advantages and disadvantages of method
Intrinsic variation of flame or difference in coefficient of absorption of fresh and reacting substance	Photoregister	Linear speed along one line on surface of charge	Direct continuous measurement	Is absent or (in the presence of illumination) is very small	Expensive and installation and also very complicated
	Movie camera	Linear speed and form of front in one lateral projection	Direct measurement; continuity is determined by relationship of burning rate and speed of filming	The same	Experiments are simple, miscounting of films is bulky
	Photocell, photoresistance	Linear speed along surface of charge	Either direct discrete or indirect continuous measurement	The same	Experiments are simple, miscounting is simple for discrete measurement
Increase of temperature and degree of ionization at front of burning	Burning thin wires	Linear speed between a small number of points in depth (or on surface) of charge	Direct discrete measurement	Increases with increase in the number of transducers	Labor-input of installation of charge rises with increase of number of transducers; miscounting is very simple
	Ionization transducers	The same	The same	The same	The same
	Thermocouple	The same	The same	The same	The same
	Thermal resistance	The same	The same	The same	The same
Increase of pressure in closed or semiclosed volume	Low-inertia transducer of pressure	Mass speed	Indirect continuous measurement	Is absent	The same
		Linear speed between a small number of points	Direct discrete measurement	Is absent during registration of only beginning and end of burning. Can be considerable during introduction of intermediate layers	During registration of only beginning and end of burning, accuracy of measurement is small

*During continuous measurement speed at any point of charge is determined; during discrete measurement the average speed between separate points of charge is determined.

**In the case of direct measurement, shift of front of burning is recorded; in the case of indirect measurement secondary phenomena (for example, secretion of pressure is closed volume) are recorded.

frequently used (a break of chain is fixed with the help of a loop oscillograph, etc.). Filming (ordinary or high-speed) is widely used. A low-inertia transducer of pressure is also used (duration of burning is determined by curve $p(t)$). In a number of works, a photoregister is used. In works (for example, in [161]), in which profile of temperature is measured with the help of thermocouples burning rate can be simultaneously determined by recordings of two thermocouples located at a known distance from each other.

In an engine usually only average speed $\bar{u}$ is measured (time τ is determined between beginning and end of burning by curve $p(t)$; $\bar{u} = \ell/\tau$ where ℓ is thickness of arch of charge). In those cases in which it is necessary to determine burning rate at different points of charge, there is used extinguishing of charge at a definite time after beginning of burning. The extinguished charge will then be measured in different sections (see, for example, [236]). Now and then there is used photographing of burning charge through a slot with a small window or through the wall of a transparent camera (made from plexiglas).

Let us note that selection of this or that method of measurement of burning rate depends on the conditions in which the experiment is carried out (laboratory installations or engine; experiments in vacuum, at atmospheric pressure or at high pressures etc.). It is also very important whether it is necessary to measure only average burning rate or burning rate in different points of charge, or to be convinced that rate is time-independent. In certain cases the properties of the mixture are essential (for example, it is inconvenient to measure burning rate of mixtures with very transparent or very dim flames by photographic methods). Naturally, it is necessary to take into account accuracy of this or that method. Finally, selection of a method can be influenced by the possibility of obtaining additional information besides measurement of burning rate (thus, for example, the movie camera permits judging the form of flame and surface of charge, luminous intensity of flame, etc.).

Let us stop in greater detail on methods of measurement of burning rate in laboratory conditions.

Bombs of constant and variable pressure. In the laboratory burning rate of small cylindrical charges is usually measured (diameter 5-15 mm and height 10-100 mm), burning from end (down from above). Inasmuch as speed of flame along free (bordering on gas) surface of charge can exceed normal burning rate, lateral surface of charge is covered with a layer of varnish, cement resin, etc., or is blasted (from bottom to top) with inert gas, or the charge is pressed into a shell of metal or plexiglas.*

At pressures higher than atmospheric pressure, experiments are conducted in hermetic vessels ("bombs"), able to sustain necessary pressure. If weight of charge necessary, arrived per unit of volume of bomb is sufficiently small so that increase of pressure p as a result of burning of charge is small as compared to initial pressure in bomb p_0 , the term "bomb of constant pressure"

*Shell should very densely adjoin charge; otherwise, there occurs "passage" of burning, i.e., flame spreads along clearance with very high speed [38].

d. In case in which Δp is comparable with p_0 or exceeds it, the term "variable pressure" is used. These terms are not strict, since in both cases the discussion concerns "bomb of constant volume" (incidentally, this correct term is used during the study of burning of gas mixtures). However, these terms are widely used in literature on burning of condensed substances and are convenient to a certain extent. In a majority of foreign papers about bomb of constant pressure, they are talking about the "Crawford bomb" or a bomb analogous to the Crawford bomb."

Constructions of constant pressure bombs are various; however, they consist of the same basic elements: body of bomb; cover (or, more rarely, two covers) of bomb; intake for supplying pressure to bomb and pressure drop; electric lead-ins of high (hundred of volts and above) voltage (for feeding heating coils, electromagnets, ignition coils, etc.) and low voltage (ends of thermocouples); small plexiglas or glass windows for optical methods of measurement;* inlets for pressure transducers. In certain cases there are also inlets for regulating liquid, any kind of handle for mechanical shift or charge or any components in bomb which are under pressure, etc.

The question of packing all bomb compounds is essential. It is attained with the help of linings. For components which are opened only now and then, both a metallic (copper, aluminum) and a soft (rubber, teflon, fiber) lining can be used. For covers soft linings are preferable.

Usually constant pressure bombs operate at $p \leq 150$ atm (pressure is supplied by compressed nitrogen from standard balloons). However, there are also constant pressure bombs calculated on pressure of 500[36], 1000 atm [42] and more, where pressure is created with the help of a gas compressor.

The usual volume of constant pressure bombs is several liters (not more than 10 l). In necessary cases a receiver is used (at $p \leq 150$ atm standard balloons can be used as a receiver). However, the faster the burning rate, the bigger should be the cross section of main lines connecting bomb with receiver, so that pressure is levelled.

As an example on Fig. 22 shows a diagram of a bomb of [B-150] (B-150) construction of the Institute of chemical physics of the Academy of Sciences of the USSR. The volume of the bomb is 2 l; the bomb has three small plexiglas windows (20 x 40 mm), four high-voltage (several hundreds of volts) inlets. There is a number of B-150 modifications (for temperature measurements and others).

*Plexiglas permits easily packing small window and has sufficiently time-independent mechanical characteristics, whereas glass must be packed very carefully and is inclined to fatigue breakdown (cases were observed in which a small glass window was destroyed at a supply of pressure a few times lower than that pressure at which it worked during a prolonged time). Conversely, optical characteristics for plexiglas are considerably worse than for glass (during packing the surface of plexiglas noticeably bulges; plexiglas easy scratches, burns, etc.).

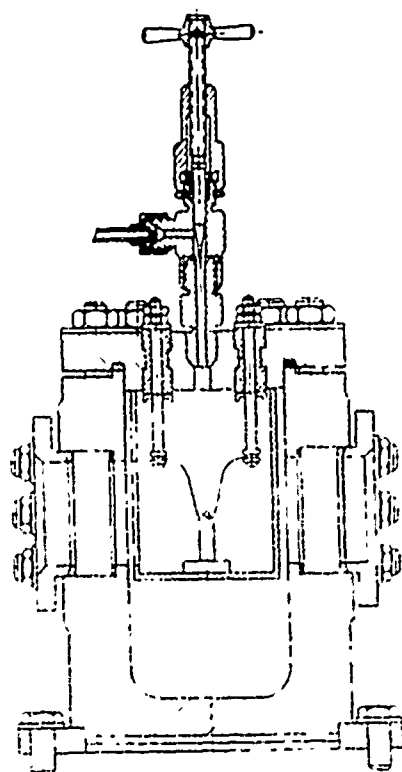


Fig. 22. Diagram of constant pressure bomb B-150.

Variable pressure bombs are the oldest device for investigation of burning of powders at high pressures. Curve $p(t)$ was measured with the help of simple mechanical transducers. Maximum pressure in bomb was determined, furthermore, on value of pressing of a copper column ("crusher"). From the form of curve $p(t)$, there can be obtained a tentative idea about dependence $u(p)$ for the compound investigated. Bombs of similar type are frequently called manometric. Maximum operating pressure in such bombs reaches several thousands of atmospheres.

In contemporary variable pressure bombs for recording curve $p(t)$ it is usual to use low-inertia piezo and strain gauges of pressure. In principle it is possible to use other methods of measurement of burning rate (burning wires and even optical methods).

As an example of the use of variable pressure bombs, it is possible to indicate work [44] (of a bomb on 4000 atm with registration of curve $p(t)$ with the help of piezotransducer; there were used charges composed of several tablets with different burning rate — bends on curve $p(t)$ allowed determining time of beginning and end of burning of every tablet). Let us stop now on certain laboratory methods of measuring burning rate in somewhat greater detail than was done at the beginning of this paragraph.

Photoregister. Photographing of flame on film continuously moving perpendicularly to the direction of propagation of flame is one of the oldest methods of measuring burning and detonation rate. The corresponding instrument in domestic literature is called a photoregister (or photorecorder). This name bears an accidental character; the principle of action of the instrument is more successfully reflected by the term, "slot camera" or "drum camera" (slit- or drum-camera) used in English literature.

There are two types. In one of them (with "drum scanning"), the lateral surface of revolving drum, but image of charge is a laborious system of coordinates; in the second (with mirror scanning) the image of the charge slips (for further detail see [1]). The first type permit obtaining a speed up to several kilometers per second. In practice the study of burning photoregisters with drum scanning are used, but the study of detonation photoregisters with mirror scanning are mainly used.

On film taken with the help of a photoregister there is a slanted line, which corresponds to the position of the front point of flame (below this line

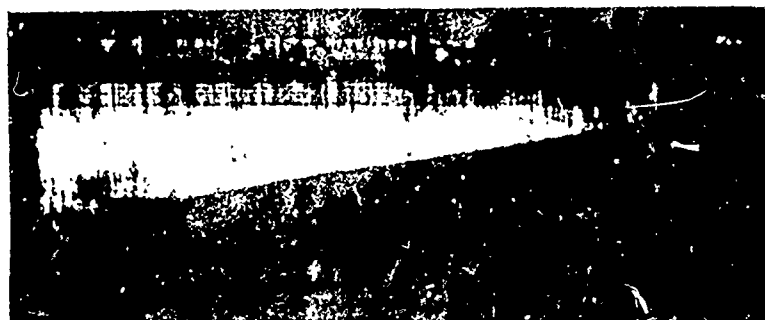


Fig. 23. Sample of photoregister recording

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the film is transparent, and above it the film is lighted by products of combustion; Fig. 23). Burning rate is calculated by the formula:

$$u = \frac{v_{\text{film}}}{k \cdot \tan \phi} \quad (99)$$

where u is burning rate, v_{film} is speed of film; k is ratio of height of charge to height of its image on film; ϕ is angle between line traced by image of front point of flame and horizontal axis (vector of linear speed of film).*

Accuracy of measurement of burning rate is higher the sharper the front of illumination on film. It is not difficult to show that the clearest front will be obtained in the case of the burning flame moving along a certain

*For calculation of the burning rate it is necessary to make an attachment to the photographic enlarger shown in Fig. 24. During the measurement the mobile rule is placed parallel to the front of illumination and the scale division drawn on the edge of the plate of the attachment is used. Value $\tan \phi$ is calculated beforehand for every scale division.

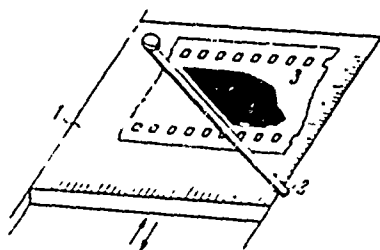


Fig. 24. Attachment for miscounting of films taken on photoregister. 1 — sliding plate; 2 — mobile rule on axis; 3 — image of film.

narrow* slot (i.e., to photograph a luminescent point or luminescent segment a straight line moving perpendicularly to the direction of motion of film).

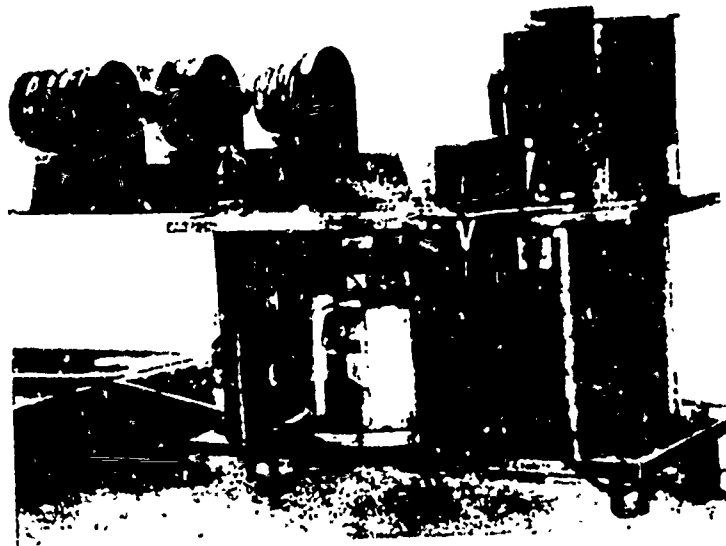
The two constructive diagrams of the optical part of a photoregister. In the one-lens diagram, the slot is located near the charge. In the two-objective diagram, the slot is located in the plane of the charge image created by the first objective. The second objective depicts the slot and intermediate image of charge on film. In the first case the front of illumination on film is obtained less clearly (since the charge and slot are in different, although close planes), but then in second case system candle-power is lower, and focusing is more complex.

Analysis of errors of measurement of burning rate with the help of a photoregister shows [162] that there is an optimum value of angle ϕ , at which measuring errors are minimal. During burning of small (height 1-2 cm) charges for a one-lens photoregister $\eta_{\text{opt}} \approx 10-15^\circ$ (for a two-objective photoregister, it is somewhat greater).

Burning rate of condensed mixtures changes over a wide range (at least from 0.1 to 100 mm/s) depending upon nature of mixture, ratio of components, pressure, etc. In order to have the possibility in every case to carry out filming at ϕ not too distant from ϕ_{OPT} , it is necessary to be able to regulate speed of film over a wide range. Therefore, photoregisters for measurement of burning rate have reduction gear with a large number of working speeds. Thus, for example, Fig. 25 shows a drum photoregister of construction of the Institute of chemical physics of the Academy of Sciences of the USSR with two-objective optical system and a set of film speeds of 1, 2, 4, 8, 16, 32, 64, 128, 256, 512 and 1024 mm/s.

Measurement of $\bar{u}$ with the help of a pressure transducer. This method permits determining interval of time τ between beginning and end of burning on oscillogram with recording of curve $p(t)$ (in both a constant and a variable pressure bomb). Then $\bar{u} = h/\tau$, is calculated where h is height of charge. The oscillogram also permits judging whether burning rate oscillations were observed. In a constant pressure bomb, it is expedient to use a piezotransducer, since it can operate as a differential transducer: while the bomb is being supplied with compressed nitrogen (the pressure of which is measured by an ordinary manometer), the piezocrystal edges of the plate are grounded; the

*Certainly, it is possible to decrease width of slot only as long as this is not limited by diffractional phenomena. However, the practical limit of width of slot can be reached still earlier because of losses of light on the slot.

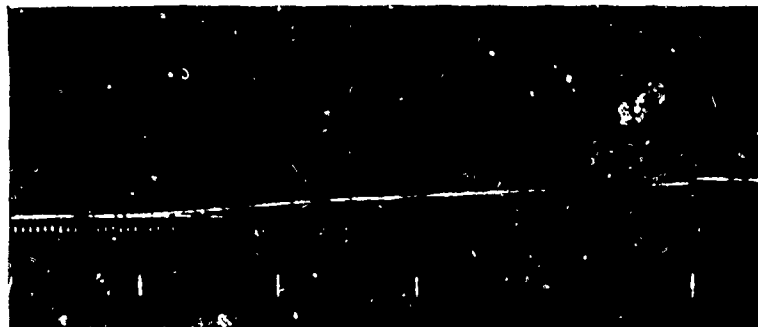


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Fig. 25. Drum photoregister with two-objective optical system for measurement of burning rate.

transducer is put into the working position before the experiment. Maximum beam deflection on oscillogram corresponds to Δp (increase of pressure as a result of combustion). Sensitivity of piezotransducer is easy to regulate at the expense of change of capacity of the condenser to which there moves an electrical charge from the piezocrystal, and also at the expense of change of ratio between area of crystal and area of rod on which pressure in bomb acts.

In order to make recording $p(t)$ more clear, to the lower fact of the charge, there is pressed a small suspension of quick-burning composition (for example, potassium picrate), and ignition is carried out by energetic ignition. In this case at the beginning and end of burning, on the curve there appear "steps" (Fig. 26).



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Fig. 26. Oscillogram with recording of curve $p(t)$. Lower ray — time (~ 50 Hz from city network); average ray — zero line. Furthermore, to it there moves timing with multiple frequency (x8 or x16 or x32 etc.) for acceleration of miscounting of films. The upper ray is recording of accretion of pressure in bomb in the course of burning.

The given method is very productive; however, in accuracy of measurement it yields to other methods of determination of $\bar{u}$, in which transducers are placed at a sufficient distance from beginning and end of charge.

Other methods of measurement of average burning rate. We already noted that the most wide-spread laboratory method of measurement of burning rate (average) is the method of burning wires. In order to introduce a wire into the charge it is possible either to drill a hole in the charge (however, for many reasons this is an inconvenient operation since in the case of a fragile charge, it is crumbled, and in the case of an elastic charge, an irregularly shaped hole is obtained; thin wires are difficult to stretch through a hole, etc.), or to compose (or to glue) the charge from several tablets, where wires are pressed between tablets (in this case it is possible to use easily very thin wires and to measure exactly vertical distance between them. However, in this case there are possible errors connected with change of speed at the time of transition of burning from one tablet to another).

The ionization transducer used in works [163-165] constitutes two wires (or needles), between which there was applied voltage of 100-200 V and between which the clearance was 1 mm. During passage of flame, ionization interval was locked, and in the chain there appeared current, which was recorded by loop oscillograph. Such transducers were pressed between first and second, second and third, etc., tablets of which the charge consisted; timing of burning is carried out just as in the case of burning wires.

In work [166] for measurement of flame propagation velocity along surface of contact of cylindrical layers of metal powder and solid oxidizer, instead of wires there were used thin (0.3-0.6 mm) quartz fibers, which reached to the surface of contact through holes drilled in the external layer. During passage of flame past a given thread, light from the flame got on the photoresistance and the signal was recorded on the loop oscillograph.

Methods of measuring $\bar{u}$ with the help of burning wires, ionization transducers, "light wires," etc., from a principle point of view, are more or less equivalent. From a methodical point of view, the first method (burning wires) is the simplest, although the second method is only a little more complex than the first. Installation of transducers in the third method is more complicated than in the first two methods. Selection of this or that method is frequently dictated by properties of the investigated system.

§ 13. Dependence of Speed of Burning on Dispersiveness of Components

Dependence of burning rate of condensed mixtures on dispersiveness of components presents essential practical interest, since it permits regulating burning rate without change of mixture ratio, and, consequently, also without change of specific impulse of fuel

Furthermore, presence of dependence $u(d)$, where d is dimension of particles of components, must be considered during adjustment of technology of preparation of condensed mixtures, so that scattering in burning rate during transition from one party of raw material to another remains within permissible limits.

dependence $u(d)$ also presents great theoretical interest, since it expresses influence of dimension factors on burning rate in the most relief. A considerable part of the most essential part of concepts about burning of condensed mixtures is based on the study of exactly this dependence.

A. Dimension of Particles of Components

In general the burning rate of condensed mixture depends both on dimension of particles of oxidizer d_{OK} and on dimension of particles of fuel d_F . However, if fuel is plastic at the time of displacement, it will form layers between crystals of oxidizer. Dimension of layers of fuel is directly proportional to dimension of particles of oxidizer ($d_F = (1/k) d_{OK}$). Consequently, in this case (which has great practical value) dependence u on disperseiveness of components is reduced to dependence $u(d_{OK})$. An analogous result will be observed for a mixture of two powdery components (easily gasified), if dimension of particles of one component is much less than the second. Finely-dispersed component will form layers the dimension of which is proportional to dimension of particles of coarsely dispersed component. If, however, finely-dispersed component is nonvolatile and does not cohere in monolithic layer, burning rate can depend both on d_{OK} and on d_F .

Till now we have implied that all particles of a given component have identical dimensions. In practice this condition can be carried out only approximately, working with narrow ("monodispersed") fractions.

At dimension of particles of more than 30-40 microns, there are used fractions obtained with the help of sieves (of brass or bronze wire or silk fabric). Fractions of type 40-50, 100-140, 300-400 microns, etc., can be considered sufficiently monodispersed. Application of narrower fractions usually inexpedient since the accuracy with which it is possible to take dependence $u(d)$ is not too high (because of differences in distribution curves of particles by dimension for every fraction; errors in uniformity of mixing of components etc.). Furthermore, preparation of very narrow fractions requires much time.

Initial powder taken for preparation of narrow screen fractions should not contain essential impurity of small (≤ 10 microns) particles, since they are very difficult to liberate during sifting. If initial powder is larger than necessary for assigned fraction, it is impossible to crush it (during splitting many trifles will be formed), and it is necessary to recrystallize it (if this is possible, of course) in such a way* as to obtain particles with a dimension close to that sought.

*If a saturated solution of $KClO_4$ or NH_4ClO_4 is cooled very fast (for example, by pouring hot solution in a thin layer on the surface of a massive metallic cuvette cooled to low temperature), small crystals will be formed. Conversely, during very slow (tens of hours) cooling of saturated solution very big (several millimeters and more) crystals will be formed.

At a dimension of particles of less than 20-30 microns, preparation of narrow fractions (methods of precipitation in fluid and gas flow and other methods) becomes a labor-consuming and unproductive operation. Therefore, at $d < 20-30$ microns there are most frequently worked with polydispersional fractions, obtained by milling on mills of different type. Nevertheless, such fractions are not infrequently characterized by a certain average effective dimension, which is most frequently calculated by value of specific surface from relationship

$$d_{\phi\phi} (cm) = 6/S_{\Sigma} (cm^2/g) \rho (g/cm^3),$$

where ρ is particle density.

Besides screen dimension (which is usually defined as arithmetic mean between dimensions of cells of sieves, with the help of which a given fraction is obtained; for example, for the fraction, * -0.140 + 0.100, average screen dimension is equal to 120 microns) and effective dimension calculated by value of specific surface, microscopic dimension is also used. In order to find average microscopic dimension, there is measured with the help of a microscope with ocular grid a sufficiently large number of particles (not less than several hundreds) in two mutually perpendicular directions and then the arithmetic mean is taken (and other methods of averaging can also be used).

For the same fraction, average microscopic dimension, as a rule, is greater than average screen dimension, since extended particles can skip through a cell of given dimension.

Besides systems with monodispersed fractions, of great practical interest are systems in which the investigated component is taken in the form of a mixture of two narrow fractions, essentially differing in dispersiveness. For such systems it is possible to investigate dependence of burning rate on the ratio between big and small fraction, on dimension of big fraction (during constant dimension of small fraction) and, conversely, on dimension of small fraction (during constant dimension of big fraction), etc. It is natural that dependence of burning rate on dispersiveness in this case is complex and less graphic.

In certain works (for example, [167]) dimension of fractions is characterized by a full curve (usually integral) of distribution of particles by dimension. Of course, this permits obtaining a more correct idea about the dispersiveness of a fraction, but until now has brought perceptible benefit during the study of dependence $u(d)$, and, finally, for every fraction there is calculated some average dimension, which appears in dependence $u(d)$.

*The minus sign (-) is taken as designating dimension of cell of sieve through which a given fraction has completely passed; the plus sign (+) is dimension cell of sieve on which a given fraction has remained.

Interval of Change of Burning Rate at the Expense of Change of Dispersiveness of Components

It is of interest, first of all, to clarify the question of how much it is possible to change burning rate at the expense of change of dispersiveness of components. This question is specially investigated in work [139].

We will designate by $\theta_* = u_0/u_\infty$ the ratio of burning rate of maximally finely dispersed mixture, $u_0 = u/d \rightarrow 0$ to burning rate of maximally coarsely dispersed mixture, $u_\infty = u/d \rightarrow \infty$. It is natural that in real conditions, range of change of dispersiveness is not infinitely large. Even in laboratory conditions the most finely pulverized fractions of oxidizer usually have dimension not less than 5-10 microns (powders of metals can be considerably smaller — as small as 0.1-0.01 micron; see, for example, [171, 172]). All the same it is practically impossible to mix components so thoroughly that nodulizing of small particles is completely avoided.

Dimension of particles in the most coarsely dispersed mixtures does not exceed 300-500 microns and only in rare cases reaches 1-2 mm (in laboratory mixtures).

Thus, in general, it is possible to realize only partially the possibility of control of burning rate at the expense of change of dispersiveness of components. Real value $\theta = u_M/u_{KP}$ (where u_M , u_{KP} is the burning rate of the most finely dispersed and the most coarsely dispersed mixture) remains less (frequently considerably less) than limiting value $\theta_* = u_0/u_\infty$.

Experimental data show that for gasified components dependence $u(d)$ is comparatively weak, and interval of change u at the expense of change d (characterized by value θ) is small. Conversely, for nonvolatile components dependence $u(d)$ is considerably stronger, and value θ is considerably larger (Table 35). In other words, at the expense of change of dimension of particles of nonvolatile component, it is possible to change burning rate much more than at the expense of change of dimension of particles of easily gasified component.

This circumstance, apparently, is completely regular. From § 6A, B it is clear that for systems with gasified components, displacement of components can still take place with sufficient speed in the zone of heating. Accordingly, burning rate to a considerable extent is determined by kinetic factors, and dependence $u(d)$ is weak (and at sufficiently small d is in general, absent since mixing is completed within limits of zone of heating).

Conversely, for systems, where one component (usually oxidizer) is gasified, and the second is nonvolatile, mixing can proceed only simultaneously with reaction. In this case burning proceeds in conditions close to diffusion conditions, and dependence $u(d)$ (where d is dimension of particles of nonvolatile component) is strong.

Table 35. Change of Burning Rate of Condensed Mixtures at the Expense of Change of Dispersiveness of Components

Mixture	z	Component, for which u(d) is investigated	Dimension of particles of component studied in microns	d_{kp}/d_m	$\rho = u_w/u_{kp}$				Literature
					5 atm	10 atm	40 atm	100 atm	
KClO ₄ - bitumen	1	KClO ₄	~10	1700	170	1,87	2,1	2,16	2,20 [137]
NH ₄ ClO ₄ - polystyrene (unagelated mixture);	1 0.5 0.2	NH ₄ ClO ₄ NH ₄ ClO ₄ NH ₄ ClO ₄	~6 ~6 ~6	230 230 230	~38 ~38 ~38	1,38 1,21 —	1,29 1,38 —	1,37 1,56 1,11	1,40 1,54 1,42 [168]
The same, wetted mixture	1 0.5	NH ₄ ClO ₄ NH ₄ ClO ₄	~6 ~6	230 230	~38 ~38	2,24 1,68	2,19 2,33	3,28 2,56	3,29 3,04 [168]
KClO ₄ - graphite	0.4	Graphite	~2	125	~62	—	—	8,6	11,0 [164]
KClO ₄ - W	~0.2 ~0.1	fungsten The same	~2,7 ~2,7	550 340	~204 126	47,5 40,7	— 11,2	44,5 33,4 (50 atm)	31,7 29,7 [139]
Fe ₂ O ₃ - Al	~1	Aluminum	0,1	550	550	25,7	26,8	16,4 (50 atm)	17,2 [139]

*See explanation in 14.

C. Form of Curve $u(d)$

In the preceding division it was noted that during change of dimension of particles a given number of times, burning rate is strongly changed in case of nonvolatile component and weakly changed in case of easily gasified component. It is natural to expect that the form of curve $u(d)$ should be different for these two cases.

For the nonvolatile component, the form of curve $u(d)$ is investigated only in work [139]. For $KClO_4$ - W mixture experiments were conducted with five different fractions of tungsten (four of which were obtained by sowing one party of tungsten powder, and the fifth, powder with dimension ~ 2.7 microns, pertained to another party). Dispersiveness of big fractions was characterized by average screen and microscope diameter; dispersiveness of small fractions was characterized by effective diameter calculated by value of specific surface ($S_{уд}$ was determined by method of air suction through a layer of powder with the help of instrument [PSKh-2] (ПСКХ-2)):

Screen fraction	-0,100	-0,100— +0,110	-0,110— +0,100	-0,010	Powder
$d_{\text{ситовой}} \mu$	—	270	120	—	—
$d_{\text{микроскопн}} \mu$	550	340	160	~ 13	—
$d_{\text{эв}} \mu$	—	—	—	~ 19	$\sim 2,7$

According to work [139], dependence $u(d)$ (more exactly $\lg u = f(\lg d)$; Fig. 27) has a plateau at "average" d . In other words, at small d (~ 3 -19

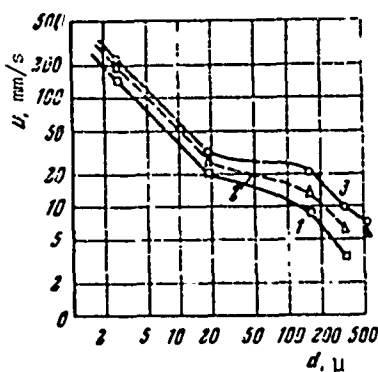


Fig. 27. Dependence of burning rate of 90% W + 10% $KClO_4$ mixture on particles of tungsten at different pressures [139]: 1 — 10 atm; 2 — 50 atm; 3 — 100 atm

microns) dependence $u(d)$ is strong ($u \sim 1/d$); at "average" d (19-160 microns) dependence $u(d)$ is weakened, and then at large d (160-550 microns) it again approaches $u \sim 1/d$. Due to the absence of other experimental data, it is not yet clear how real weakening of dependence $u(d)$ is at "average" d .

The form of curve $u(d)$ for particles of gasified components has been investigated in much greater detail (see [137, 141, 146, 169, 170] and others).

First of all, it is necessary to note that there is a "normal" curve

$u(d)$ for mixtures, the composition of which is not too far from stoichiometry, and "anomalous" curve $u(d)$ for mixtures with a very large surplus of fuel (and, possibly, also for mixtures with a very small percentage of fuel, i.e., with a very large surplus of oxidizer).

We will examine at first "normal" curve $u(d)$. In work [137] on example of stoichiometrical mixture KClO_4 - bitumen it was shown that at pressures which are not too high, (for given mixture up to 5 atm), curve $u(d_{\text{OK}})$ has an S-shaped form (Fig. 28): for gasified component burning rate weakly

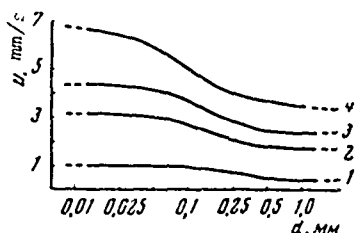


Fig. 28. Dependence of burning rate of stoichiometrical KClO_4 + bitumen mixture on dimension of particles of oxidizer at different pressures [137]: 1-1 [atm(abs.)]; 2-3 [atm(abs.)]; 3-5 [atm(abs.)]; 4-10 [atm(abs.)].

depends on dispersiveness at small d_{OK} ; then at "average" d_{OK} burning rate essentially drops with increase in d_{OK} , but at large d_{OK} dependence $u(d)$ is again weakened. The left plateau (at sufficiently small d), apparently, is connected with the fact that displacement of components is completed in zone of heating, and burning takes place in kinetic conditions (see § 8A).

With increase in pressure (and in conformity with burning rate), the left plateau on experimental curves $u(d)$ vanishes. It is possible that it would also be observed and at high pressures, if experiments were conducted with still more finely dispersed mixtures (in other words, the plateau can be observed both at low and at high pressures, but it is shorter the higher the pressure).

The presence of a plateau at $d < d_{\text{min}}$ is also confirmed by the results of work [123], according to which there is a definite value $u_{\text{min}} \approx 0.35-0.45$ mm/s (burning rate was changed at the expense of change in p at several values α) such that at $u < u_{\text{min}}$ the small (74-105 microns) and the big (297-420 microns) fractions of NH_4ClO_4 burned (in the flow of methane) with the same speed.

The right plateau (at large d) is connected with the fact that increase in d above certain limits no longer affects processes occurring in the zone of influence. Out of the number of works (besides work [137]) in which weakening of dependence $u(d)$ was observed at large d , we will mention work [146]. For a composition (65% NH_4ClO_4 , 24% unsaturated polyester, 10% nitroglycerine, 1% additions) experimental points were approximated by formulas $u \sim d^{-n}$, where value n was:

d	u	
	p = 1 atm	p = 3 atm
less than 150 μ	0,57	0,59
More than 150 μ	0,20	0,074

Let us consider now the form of curve $u(d)$ at a large surplus of fuel. In work [170] there are conducted experiments with mixtures of NH_4ClO_4 * with polystyrene (<100 microns) at $\alpha = 0.15$; 0.2 and (for comparison $\alpha = 1$, and also with plexiglas (~3 microns) at $\alpha = 0.2$ and (for comparison) $\alpha = 1$. It turned out that for mixtures with a large surplus of fuel, burning rate increases with decrease in d only up to a certain limit, but then at a certain value of d passes through a maximum and starts to decrease (Figs. 29b and c, 30).

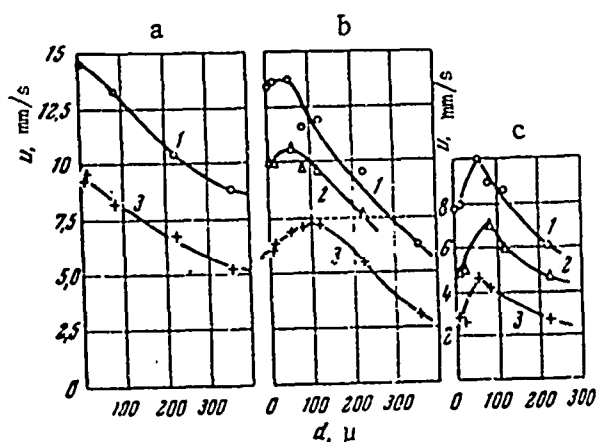


Fig. 29. Dependence of burning rate at different pressures for nongelated mixtures of NH_4ClO_4 + polystyrene (<100 microns) on dimension of NH_4ClO_4 particles [170]. a — $\alpha = 1.0$; b — $\alpha = 0.2$; c — $\alpha = 0.15$. 1 — 100 atm; 2 — 70 atm; 3 — 40 atm.

Paradoxical dependence $u(d)$ for mixtures with large surplus of fuel can be explained, if the fact is considered that burning rate is determined, not by the whole zone of transformation of components, but only by a certain part of it adjacent to the surface of charge (see § 10B).

*For NH_4ClO_4 are taken s. recn fractions 320-400, 140-320, 100-140, 63-100, 50-63 and <50 microns, and also fractions ~17 microns (washed in porcellain mill) and ~5 microns (washed in vibrating mill). Equivalent diameter of two last fractions is calculated by value $S_{y\mu}$, measured on instrument PSKh-2.

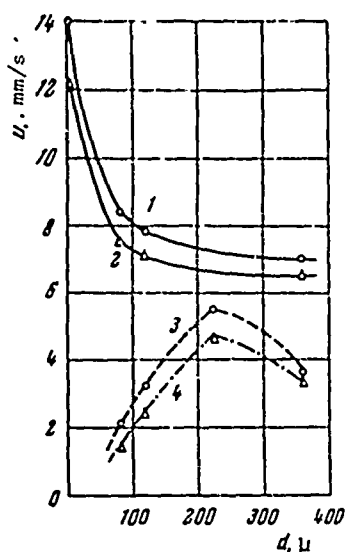


Fig. 30. Dependence of burning-rate at different pressures for nongelated mixtures of NH_4ClO_4 + plexiglas (~ 3 microns) on dimension of NH_4ClO_4 particles [170] 1, 2 - $\alpha = 1$; 3, 4 - $\alpha = 0.2$; o - 100 atm; Δ - 70 atm.

For mixtures studied in the present work, components at first are gasified and only then interreact. At sufficiently small d the ratio of components in the gas phase is the same as in the initial mixture, i.e., reacting mixture is strongly ballasted by surplus of fuel, and burning rate is low.*

However, with increase of dimension of particles of oxidizer within limits of zone affecting burning rate only a certain part of the initial components can be gasified and react. Gasification of fuel (a strongly endothermic process) will lag behind gasification of NH_4ClO_4 (decomposition of NH_4ClO_4 is accompanied by formation of flame of products of decomposition of $\text{NH}_3 + \text{HClO}_4$ and goes on with liberation of heat; see § 10).

Consequently with increase in d_{OK} the mixture reacting in the zone of influence is progressively less and less ballasted by surplus of fuel. Accordingly, burning rate increases, but only until this is ended by lowering of heat emission as a result of decrease of quantity of substance reacting in zone of influence and increase of expenditures of heat on heating of particles of fuel and oxidizer reacting far from zone of influence. Thus, for mixtures with a large surplus of fuel, curve $u(d)$ should have a maximum.

Conversely, for stoichiometrical mixtures, both examined processes (1 - decrease of fraction of substance reacting in zone of influence; 2 - change of composition of gas phase in zone of influence) act according to increase of d_{OK} in the direction of lowering of burning rate, since for stoichiometrical mixture, lag in gasification of fuel impoverishes reacting mixture and lowers its temperature.

*A very finely dispersed ($d_{OK} \approx 5$ microns) mixture of NH_4ClO_4 + plexiglas at $\alpha = 0.2$, cannot, in general, be ignited (in the 5-100 atm range).

it is necessary to make the following remark. At sufficiently large surplus of fuel, in region of small d there occurs deceleration of burning (with decrease in d). It is natural that at somewhat smaller surplus of fuel, in region of small d there can be observed a plateau (however, its origin will be quite other than in the case examined in § 8A). It is possible that this is exactly the way to explain the presence of plateau (long enough even at 50-70 μ m) on curves $u(d)$ for the Thiokol composition in work [178] (Fig. 31).

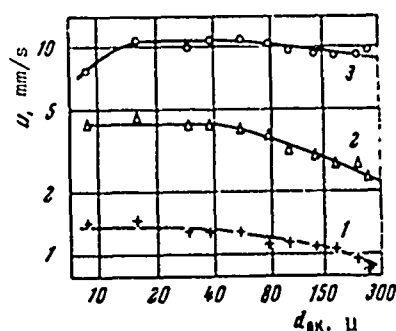


Fig. 31. Dependence of burning rate of oxidizer for Thiokol composition at different pressures [178]:
1 — 1.2 atm; 2 — 7 atm; 3 — 112 atm.

Apparently, anomalous curve $u(d)$ can be observed also for mixtures with a very small percentage of fuel (i.e., with a large surplus of oxidizer). At least in work [123] during burning of a layer of NH_4ClO_4 , particles through which methane was ventilated, essential weakening was observed of dependence $u(d_{0K})$ with decrease in expenditure of methane. The ratio of burning rates of the smallest fraction investigated (74-105 microns) and the biggest fraction investigated (297-420 microns) was:

α	27,2	13,6	4,53	2,72	1,95
$u_{\alpha}/u_{1,\mu}$	1,0	1,22	1,25	1,25	1,27

Thus, in this case, at a very small percentage of fuel there is a very long plateau on curve $u(d_{0K})$ (in that interval of d , where for mixtures not too far from stoichiometry, u noticeably increases with decrease in d).

Meanwhile in work [173] it is shown that mixtures of finely-dispersed NH_4ClO_4 with volatile powdery fuel at a very small percentage of fuel have a burning rate lower than pure NH_4ClO_4 (see also § 19). In other words, addition of a small percentage of fuel to finely dispersed NH_4ClO_4 lowers burning rate. It is possible that with increase in d (and other equal conditions), this lowering will be less. If this is the case, dependence $u(d_{0K})$ will be anomalous (with increase in d , absolute velocity of burning will increase somewhat). This was not checked experimentally.

D. Dependence $u(d)$ for Polydispersional Mixtures

Of considerable practical and theoretical interest is burning of systems in which oxidizer is taken in the form of a mixture of two (or more) fractions essentially differing from each other in dispersiveness.

If burning rate was simply determined by value of specific surface of components, then, for example, for a system containing 50% very small ($d \sim d_{\min}$) and 50% very big fraction of oxidizer, burning rate u_{CM} would equal approximately $(u_M + u_{KP})/2$, where u_M , u_{KP} are burning rates of a system with finely dispersed oxidizer and a system with coarsely dispersed oxidizer, respectively.

However, experiments conducted in works [156, 168] showed that this trivial case is carried out for only part of the systems (see composition 2 in Table 36).

Regarding, however, remaining compositions, for some of them (composition 3) u_{CM} is close to u_M or even exceeds u_M (composition 1 at 70 and 100 atm). Conversely, for other compositions u_{CM} is close to u_{KP} (composition 4) or even less than u_{KP} (composition 5 at 40 and 100 atm).

Let us note that the relationship between u_M , u_{CM} and u_{KP} can be conveniently characterized by parameter $Y = \frac{u_{CM} - u_{KP}}{u_M - u_{KP}}$. For the cases examined above, value Y is equal to:

$$\begin{array}{lll} u_{CM} \geq u_M & u_{CM} \leq u_{KP} & u_{CM} = \frac{u_M + u_{KP}}{2} \\ Y \geq 1 & Y \leq 0 & Y = 0,5 \end{array}$$

In order to explain why, in some cases, u_{CM} is close to u_M , and in other cases is close to u_{KP} , we will examine structure of zone of burning. Compositions with doubly dispersed oxidizer are essentially nonuniform: in them there is a grid of crystals of big oxidizer, the intervals between which are filled with comparatively uniform mixture of fuel with small oxidizer at a ratio of components equal to $\alpha/2$.

If the burning rate of this uniform mixture $(u_M)_{\alpha/2}$ is sufficiently great, flame spreads in intervals between big crystals of oxidizer. Burning rate of composition with mixed oxidizer u_{CM} turns out to be approximately equal to $(u_M)_{\alpha/2}$. If $(u_M)_{\alpha/2} \geq u_M$, then $u_{CM} \approx u_M$. The presence of big oxidizer here only lowers burning rate. Conversely, if $(u_M)_{\alpha/2}$ is close to u_{KP} , the presence of big oxidizer can increase burning rate. Finally, if uniform mixture in intervals between big crystals does not burn by itself or has a very low burning rate, u_{CM} will be close to u_{KP} and can be even lower than u_{KP} (but not less than $(u_{KP})_{\alpha/2}$).

Table 36. Burning Rate of Compositions on the Basis of NH_4ClO_4 with Small (~5 Microns), Big (140-320 Microns) and Mixed (50% Small + 50% Big) Oxidizer

number of composition	Fuel	Method of preparation of mixture	α	Dispersiveness of oxidizer	u, mm/s				
					10 atm	25 atm	50 atm	70 atm	100 atm
1	Polystyrene (<100 microns)	Nongelated*	1	Big	3,8	5,1	6,8	9,1	10,4
				Mixed	4,8	7,2	9,1	12,2	15,1
				Shallow	4,9	7,4	9,3	12,0	14,6
				Y	0,91	0,92	0,92	1,07	1,12
			0,5	Shallow	5,4	7,8	10,6	14,0	16,6
2	Polystyrene	Gelated*	0,7	Big	4,2	6,6	7,6	10,3	12,1
				Mixed	7,2	12,2	16,6	22,2	29,2
				Shallow	9,9	17,1	23,4	35,2	42,4
				Y	0,52	0,53	0,57	0,48	0,56
			0,35	Shallow**	6,2		14,0		26,5
3	Plexiglas	Gelated	2	Big	2,7	4,4	5,3	7,5	8,0
				Mixed	4,9	7,9	10,6	12,9	15,8
				Shallow	5,4		10,7		16,2
				Y	0,82		0,98		0,95
			1	Shallow	7,0	11,1	14,5		22,8
4	Plexiglas (~3 microns)	Nongelated	1	Big	3,2	4,7	5,2		7,0
				Mixed	4,0	5,3	5,8	7,3	7,5
				Shallow	5,7	8,1	9,1		12,7
				Y	0,32	0,18	0,15		0,09
			0,5	Shallow	3,3	4,2	3,9	4,0	6,0
5	Plexiglas	Nongelated	0,7	Big	3,5	4,8	5,7		8,2
				Mixed	4,0	5,2	5,6	6,3	7,4
				Shallow	4,5	5,4	6,2	7,8	8,7
				Y	0,50	0,67	-0,2		-1,6
			0,35	Shallow					

Not mountaine

*Nongelated mixture was prepared by mixing powdery components. Gelated mixture was prepared in the same way, but was then flooded by solvent (dichlorethane), sustained during mixing for twenty-four hours and dried. During gelatinization fuel was distributed in the form of films on the surface of particles of oxidizer.

**Data are obtained by interpolation from curve u(α).

Thus, the ratio between u_{CM} , u_M and u_{kp} is determined by the ratio between $(u_M)_{\alpha/2}$, u_M and u_{kp} . On Fig. 32 there is shown the general form of curve

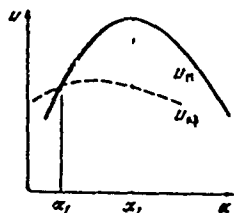


Fig. 32. General form of dependence $u(\alpha)$ for dispersed (u_M) and coarsely dispersed (u_{kp}) mixtures.

$u(\alpha)$. Obviously, inequality $(u_M)_{\alpha/2} > u_M$ (and, accordingly, $Y \geq 1$) can take place at $\frac{\alpha}{2} > \alpha_2$, i.e., on the right branch of curve $u(\alpha)$. Equality $(u_M)_{\alpha/2} \approx u_M$ can take place at $\alpha > \alpha_2$. In this case points $(u_M)_{\alpha/2}$ and u_M lie to the left and to the right of the maximum respectively. Finally, inequality $(u_M)_{\alpha/2} < u_{kp}$ is knowingly fulfilled at $\alpha \leq \alpha_1$.

Besides experiments with mixed oxidizer containing 50% big and 50% small fraction, in work [168] there were conducted experiments with mixed oxidizer containing 20% big and 80% small fraction. It turned out that $(u_{CM})_{20:80}$ is everywhere almost equal to (but is slightly less than) burning rate of uniform mixture $(u_M)_{0.8\alpha}$ in intervals between big crystals. This will agree well with considerations stated above.

§ 14. Dependence of Speed of Burning on Ratio of Components

Burning rate of condensed mixtures essentially depends on the ratio between fuel and oxidizer (α).

Curve $u(\alpha)$ has its maximum at a certain value $\alpha = \alpha_{u_{max}}$, and to left and right of maximum, burning rate decreases, first gradually, and then more and more steeply. The left branch of curve $u(\alpha)$ (surplus of fuel) breaks off at a certain sufficiently small value α (rich limit). Regarding the right branch for oxidizers not able to burn in pure form (for example $KClO_4$), there also exists a poor limit, whereas for oxidizers (for example, NH_4ClO_4), capable (at a given pressure) of independent burning, the poor limit is absent.*

*From § 19 we see that small additions of certain fuels to ammonium perchlorate can lead to damping of burning at those pressures at which burning of pure NH_4ClO_4 is completely stable. In these cases in region of lead mixtures, there are two limits, between which burning does not go on.

A. Position of Maximum Burning Rate

From § 1B it is clear that for gaseous mixtures (both air and, all the more so, oxygen) maximum of burning rate lies near stoichiometry (for air mixtures $\alpha_{u_{\max}} = 0.8-1.1$). The only exception is mixtures with hydrogen and carbon monoxide, for which $u_{\max}$ is essentially displaced in the direction of surplus of fuel. At least in the case of hydrogen mixtures, such displacement is connected with the fact that speed of flame is to a considerable extent determined by diffusion of active particles (in this case mainly hydrogen atoms) in fresh mixture.

For condensed mixtures with gasified components, $u_{\max}$ lies near stoichiometry [164, 169, 141, 151, 175-177]. Thus, in works [164, 175] for finely dispersed mixtures of NH_4ClO_4 (or KClO_4) with polyformaldehyde, plexiglass, benzoic acid, and bitumen, $u_{\max}$ (at $p \leq 100$ atm) lay at $\alpha = 0.7-1.0$ (on Fig. 33 data

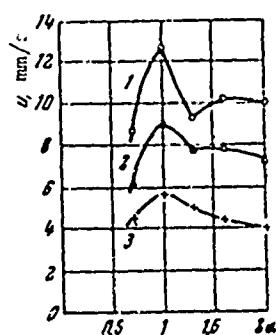


Fig. 33. Dependence $u(\alpha)$ for nongelated mixture of NH_4ClO_4 (~5 microns) + plexiglas (~3 microns) at different pressures [175].
1 — 100 atm; 2 — 40 atm; 3 — 10 atm.

are given for a finely divided NH_4ClO_4 plexiglas mixture). An analogous result is obtained in work [177] for mixtures of NH_4ClO_4 with a number of solid and liquid fuels (Table 37) and also in work [176] for a layer ($\delta = 0.51$) of

Table 37. Dependence $u(\alpha)$ for Mixtures of NH_4ClO_4 with Different Fuels ($p = 1$ [atm(abs.)]) [177]

Fuel	d_{rop}, μ	d_{ox}, μ	$u, \text{mm/s}$					
			$\alpha = 1.67$	$\alpha = 1.25$	$\alpha = 1.0$	$\alpha = 0.83$	$\alpha = 0.71$	$\alpha = 0.62$
Paraformaldehyde	<75	102-250	0.865	0.895	0.955	0.985	0.91	0.90
Urotropine	<100	102-250	0.56	0.77	0.93	0.95	0.91	0.86
Maleicanhydride	<100	102-250	0.65	0.74	0.80	0.79	—	—
Methyl methacrylate (monomer)	Liquid	102-250	0.94	0.97	0.96	0.93	0.86	0.79
		250-500	0.83	0.90	0.91	0.87	0.82	0.77

Note. Semibold type collects maximum value of burning rate.

powdery NH_4ClO_4 (250-540 microns), through which there were blasted CH_4 , H_2 , C_2H_2 , C_2H_4 , C_3H_8 and C_5H_{12} . In particular, for methane (and $\text{CH}_4 - \text{N}_2$ mixture) there is obtained:

Mixture	$m, \text{g}/\text{cm}^2 \cdot \text{s}$				
	$\alpha = 2$	$\alpha = 1$	$\alpha = 0,667$	$\alpha = 0,5$	$\alpha = 0,4$
CH_4	0,11	0,123*	0,112	0,099	0,087
90% $\text{CH}_4 + 10\% \text{N}_2$	0,096	0,11*	0,10	0,087	0,074
80% $\text{CH}_4 + 20\% \text{N}_2$	0,080	0,093*	0,085	0,074	0,063

*See note to Table 37.

With increase of dimension of particles of components, maximum burning rate can be displaced in the direction of surplus of fuel (see Fig. 33 for finely divided and Fig. 34 for coarsely divided NH_4ClO_4 - plexiglas mixture

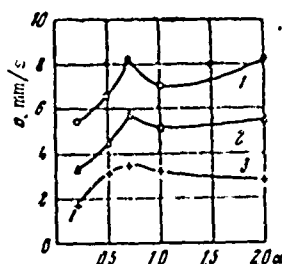


Fig. 34. Dependence $u(\alpha)$ for nongelated mixture of NH_4ClO_4 (140-320 microns) + plexiglas (~3 microns) at different pressures [175]. 1 - 100 atm; 2 - 40 atm; 3 - 10 atm.

and also data for finely divided and coarsely divided NH_4ClO_4 - methylmethacrylate mixture in Table 37.

Pressure weakly affects position $u_{\max}$ for mixtures based on NH_4ClO_4 . Conversely, for mixtures based on KClO_4 with increase in pressure, $u_{\max}$ noticeably shifts in the direction of surplus of fuel (for example, for KClO_4 - urotropine mixture at 10 atm $\alpha_{u_{\max}} \approx 0.9$, and at 50 atm $\alpha_{u_{\max}} \approx 0.5$).

If for mixtures with gasified components, $u_{\max}$ lies near $\alpha = 1$, then during transition to nonvolatile fuel, $u_{\max}$ essentially shifts in the direction of surplus of fuel. Thus, in works [164, 175] for mixtures based on KClO_4 at 30-100 atm the following value of $\alpha_{u_{\max}}$ is obtained.

Dextrin 0.9
Graphite 0.4
Tungsten <0.1

Table 38. Lowering of Burning Rate $u/u_{\max}$ at Assigned Deviation $\alpha/\alpha_{u_{\max}}$ from Composition Corresponding to Maximum Burning Rate Comparison of Finely Divided and Coarsely Divided Mixtures Based on NH_4ClO_4 . There are Given Values $u/u_{\max}$, Averaged for the Interval, 5-100 atm. In Those Cases when $u/u_{\max}$ Essentially Depends on Pressure, Values are Given a Certain Fixed p

Fuel	$\alpha/\alpha_{u_{\max}} = 2.0$	$u/u_{\max}$									
		1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8
Plexiglas* (~3 μ) [175]	$d_{\text{OK}} = \sim 5 \mu$ $d_{\text{OK}} = 140-320 \mu$	0.72 0.70	0.71 0.91	0.85 0.94	—	—	—	—	—	—	—
Pyrex*** [175]	$d_{\text{OK}} = \sim 5 \mu$ $d_{\text{OK}} = 140-320 \mu$	0.74 0.89	0.88 0.91	0.92 0.92	—	—	—	—	—	—	—
Polystyrene*** [175]	$d_{\text{OK}} = \sim 5 \mu$ $d_{\text{OK}} = 140-320 \mu$	—	—	0.93 0.92	—	—	—	—	—	—	—
$\text{C}_{11}\text{H}_8\text{O}_2$ (mono- mer)*** [177]	$d_{\text{OK}} = 102-250 \mu$ $d_{\text{OK}} = 250-500 \mu$	0.875 0.86	0.93 0.92	0.97 0.94	0.99 0.965	1.0 1.0	0.955 1.0	0.84 0.96	—	—	—
$\text{Al} + \text{Fe}_2\text{O}_3$ ** [139]	$d_{\text{Al}} \approx 4 \mu$ $d_{\text{Al}} \approx 160 \mu$	—	—	—	0.89	—	—	0.78 0.99	—	—	—

*Nongelated mixture.

** $p = 100$ atm.

***Gelated mixture.

**** $p = 1$ [atm(abs.)].

Table 39. Lowering of Burning Rate $u/u_{\max}$ at Assigned Deviation $\alpha/\alpha_{u_{\max}}$ from Composition Corresponding to Maximum Burning Rate. Comparison of Volatile and Nonvolatile Fuels

Смесь n)	Давление, атм o)	u/u _{max}										Литература p)
		$\alpha^2 u_{\max} = 2,0$	1,6	1,4	1,2	1,0	0,8	0,6	0,4	0,2		
a) NH ₄ ClO ₄ — полипропилен (<100 мк)	5—100	—	—	0,94	—	1,0	—	0,96*	0,89*	0,66*	[175]	
b) KClO ₄ (мелк.) — декстрин (мелк.)	5—100	—	0,85	0,88	0,90	1,0	0,90	0,76	—	—	[175]	
c) KClO ₄ (мелк.) — графит (1—3 мк)	5—100	—	0,58	0,73	0,87	1,0	0,94	—	—	—	[175]	
d) Fe ₂ O ₃ (мелк.) — Al (~3 мк)	100	—	—	—	0,875	1,0	0,95	0,78	—	—	[139]	
e) HClO ₄ (газ) — N ₂ — CH ₄	1 (210° C)	—	—	0,89	—	1,0	0,90	0,735	—	—	[149]	
f) HClO ₄ (газ) — CO	1 (210° C)	0,735	0,81	0,84	—	1,0	0,955	—	—	—	[149]	
g) NH ₄ ClO ₄ (140—320 мк) — плексиглас (~3 мк)	5—100	0,90	0,91	0,94	—	1,0	0,93	0,74*	0,68*	—	[175]	
h) NH ₄ ClO ₄ (76—104 мк) — полистирол (<76 мк)	70	0,94	—	—	—	1,0	—	0,96	0,87	—	[141]	
i) NH ₄ ClO ₄ (102—250 мк) — параформальдегид (<75 мк)	1	0,875	0,89	0,92	0,975	1,0	0,95	0,73	—	—	[177]	
j) NH ₄ ClO ₄ (102—250 мк) — уротропин (<100 мк)	1	0,59	0,76	0,875	0,98	1,0	0,95	—	—	—	[177]	
k) NH ₄ ClO ₄ (102—250 мк) — малеиновый ангидрид (<100 мк)	1	0,75	0,85	0,90	0,95	1,0	0,95	—	—	—	[177]	
l) NH ₄ ClO ₄ (250—540 мк) — CH ₄	1	0,902	—	—	—	1,0	—	0,87	0,707	—	[176]	
m) KClO ₄ (мелк.) — W (340 мк)	100	0,74	—	—	—	1,0	—	0,91	—	—	[139]	

* p — 100 атм.

KEY: a) NH_4ClO_4 — polypropylene (<100 microns); b) KClO_4 (finely divided) — dextrin (finely divided); c) KClO_4 (finely divided) — graphite (1-3 microns); d) Fe_2O_3 (finely divided) — Al (~3 microns); e) HClO_4 (gaseous) — N_2 — CH_4 ; f) HClO_4 (gaseous) — CO; g) NH_4ClO_4 (140-320 microns) — plexiglas (~3 microns); h) NH_4ClO_4 (76-104 microns) — polystyrene (<76 microns); i) NH_4ClO_4 (102-250 microns) — paraformaldehyde (<75 microns); j) NH_4ClO_4 (102-250 microns) — urotropin (<100 microns); k) NH_4ClO_4 (102-250 microns) — maleic anhydride (<100 microns); l) NH_4ClO_4 (250-540 microns) — CH_4 ; m) KClO_4 (finely divided) — W (340 microns); n) Mixture; o) Pressure, atm; p) Literature.

extrin is a gasified fuel, and tungsten is a nonvolatile fuel (regarding
 quite, it a definite role is played by CO formation on the surface
 of particles with subsequent burning of CO in volume).

In work [179] burning is studied of a large number of mixtures with metallic
 fuel 1 [atm(abs.)]. In all cases $u_{\max}$ will shift in the direction of surplus
 of fuel. In the series of fuels, Fe - Mn - Mo, the biggest shift, $u_{\max}$, is
 observed for molybdenum, which is least volatile (boiling point is for
 Mn ~ 2150°C, Fe ~ 2740°C, Mo ~ 4800°C).

Thus, for example, for mixtures based on KMnO_4 there is obtained:

Fuel	Mn	Fe	Mo
% of fuel when			
$u_{\max}$	45	55	76
$q_{\max}$	45	35	30
$\alpha_{u_{\max}}$	1.0	0.44	0.136*

According to [139], increase of dimension of particles of aluminum in
 Al - Fe_2O_3 mixture displaces $u_{\max}$ in the direction of surplus of fuel: so
 that at $d_{\text{Al}} \approx 4$ microns, maximum burning rate lies at $\alpha \approx 0.8$, and at
 $d_{\text{Al}} \approx 160$ microns, burning rate continues to rise slowly, at least up to
 $\alpha = 0.3$.

Results connected with position of maximum on curve $u(\alpha)$, can be explained,
 proceeding from ideas about zone of influence. We have already noted that
 for mixtures with gasified components, value α in gas phase within limits
 of zone of influence will equal value α in initial composition only for sufficiently
 finely divided mixtures. With increase of dimension of particles of components,
 value α in gas phase will be changed in the direction of surplus of that component
 which is easier to gasify. For examined mixtures such a component, apparently,
 is the oxidizer (see § 6, 8, 10B). Consequently, gas phase within limits
 of zone of influence for coarsely divided mixtures contains more oxidizer than
 initial mixture. Accordingly, less fuel is contained in zone of influence
 of coarsely divided mixtures than in initial mixture.

By this effect it is possible to explain why with increase of dimension
 of particles of components, maximum of burning rate $u_{\max}$ is displaced in the
 direction of surplus of fuel. Actually the more coarsely divided the mixture,
 the more surplus fuel must be created in initial mixture, so that composition

*Value $\alpha_{u_{\max}}$ is calculated on the assumption that maximum heat of burning
 is attained at $\alpha = 1$.

of gas phase in zone of influence remains constant (thus, corresponding to the maximum speed of reaction).

An explanation very close in meaning can be given in connection with shift of $u_{\max}$ in the direction of fuel surplus during transition from volatile to nonvolatile fuel. Actually, the less volatile the fuel, the greater the surplus of it must be created in the zone of influence to ensure identical speed of reaction (calculated, for example, by speed of consumption of oxidizer). Of no less essence is another circumstance: in case of gasified fuel, expenditures of heat on its heating, decomposition and heating of products of gasification are great. Therefore, a surplus of gasified fuel which is still not too great (especially finely divided fuel) already starts to lower burning rate essentially. For nonvolatile fuel expenditures for gasification are absent, and, therefore, only a very great surplus of fuel starts to lower burning rate.

B. Lowering of Burning Rate With Deviation of Mixture Ratio from $\alpha_{u_{\max}}$

As mixture ratio deviates from $\alpha_{u_{\max}}$ (i.e., from a composition corresponding to maximum burning rate), curve $u(\alpha)$ drops at first at a rather mild slope and then more and more steeply. This fall in burning rate will be characterized by the ratio $u/u_{\max}$, at a definite $\alpha/\alpha_{u_{\max}}$. Using the data of works examined in the preceding division, the following things can be concluded.

1. In all cases studied, surplus (as compared to $\alpha_{u_{\max}}$) of fuel more weakly lowers burning rate of coarsely divided mixtures and more strongly lowers burning rate of finely divided mixtures. In other words, value $u/u_{\max}$ (at a given $\alpha/\alpha_{u_{\max}} < 1$) for coarsely divided mixtures is larger than for finely divided mixtures (Table 38). This result is obvious from the point of view of ideas about zone of influence expounded at the end of the preceding division. The more coarsely divided the mixture, the smaller the quantity of excess fuel is gasified in it and the nearer to stoichiometry is the ratio of components in the gas phase (in the case of nonvolatile fuel, increase in d leads to decrease in thermal losses on heating of excess fuel).

As regards surplus of oxidizer ($\alpha/\alpha_{u_{\max}} > 1$), here dependence $u/u_{\max}$ on degree of dispersion less is expressed.

2. Systematic dependence $u/u_{\max}$ on volatility of fuel is not revealed, i.e., at coordinates $(u/u_{\max}, \alpha/\alpha_{u_{\max}})$ data for condensed mixtures with volatile and nonvolatile fuel, for "hybrid mixtures" (particle NH_4ClO_4 , burning in flow of methane etc.) and even for homogeneous gas mixtures are grouped approximately around the same curve (Table 39; see also Table 38, 6 and 7).

however, it is necessary to emphasize that we are concerned with deviation from $\alpha_{u_{\max}}$ (i.e., from composition with maximum burning rate).

While (as can be seen from the preceding division) actual value $\alpha_{u_{\max}}$ is absolutely different for volatile fuels ($\alpha_{u_{\max}} \approx 1$) and nonvolatile fuels ($\alpha_{u_{\max}}$ lies at great surplus of fuel). If, however, ratio $u/u_{\alpha=1}$ is calculated, i.e., how burning rate changes during deviation from stoichiometrical composition is examined, influence of volatility will be very strong (for example, for mixtures with plexiglas during introduction of fuel surplus, value $u/u_{\alpha=1}$ will start to drop rapidly, and, for mixtures with tungsten, will essentially increase up to $\alpha < 0.1$).

3. According to work [216], at high initial temperature of charge, surplus of fuel lowers burning rate more weakly than at ordinary temperature. In other words, value $u/u_{\max}$ (at assigned $\alpha/\alpha_{u_{\max}} < 1$) increases with increase in T_0 . An analogous, but a less expressed effect is observed during surplus of oxidizer. Thus, for example, for gelatinized mixture of NH_4ClO_4 (~10 microns) + polystyrene at 40 atm, the following data were obtained:

$T_0, ^\circ\text{C}$	$u/u_{\max}$		$T_0, ^\circ\text{C}$	$u/u_{\max}$	
	$\alpha/\alpha_{u_{\max}} = 0.5$	$\alpha/\alpha_{u_{\max}} = 1.0$		$\alpha/\alpha_{u_{\max}} = 0.5$	$\alpha/\alpha_{u_{\max}} = 1.0$
15	0.21	0.43	~90	0.37	0.45
~60	0.22	0.42	135	0.41	0.57

§ 15. Dependence of Burning Rate on Pressure

Dependence $u(p)$ is the most important dependence* for solid fuels used in engines of different types. And it has essential value for pyrotechnic mixtures.

For condensed mixtures (just as for homogeneous explosives and homogeneous gas mixtures) real curve $u(p)$ is usually approximated by exponential function (2) $u = bp^v$. Formula (2) was still used at the end of the Nineteenth Century

*In literature on internal ballistics (see, for example, [191]), dependence $u(p)$ is frequently called the "law of burning," or the "law of burning rate."

by V'yel', and since then has been widely propagated. It is convenient for ballistic calculations. In particular, for pressure in combustion chamber of engine (under calculated conditions) we will obtain:

$$p_k = \left(\frac{\rho b}{A} \frac{S}{S_{kp}} \right)^{\frac{1}{1-\nu}}, \quad (100)$$

where ρ is density of fuel; A is coefficient of expenditure; S is surface of burning; S_{kp} is area of critical section of nozzle. From (100) it is clear that burning in an engine is stable only at $\nu < 1$ (see also [194] and others).

Application of more complex expressions of type $u = a + bp$, $u = a + bp^\nu$, and also (96) instead of (2) is not justified (see § 2B); when it is necessary, one should split real curve $u(p)$ into sections and select for each of them coefficients in formula (2).

The majority of experimental data concerning dependence $u(p)$ pertain to the interval of pressure from 1 [atm(abs.)] to 100-200 atm. We will examine separately data (very scanty) obtained at $p < 1$ [atm(abs.)] (division D) and at a pressure from several hundreds to several thousands of atmospheres (division E).

A. Form of Curve $u(p)$

The form of dependence $u(p)$ can be very different for condensed mixtures (however, it can as well be for homogeneous explosives [VV] (BB); see Sections 2; 5). With increase of pressure, burning rate is able:

I — to increase monotonically. This type of curve $u(p)$ is observed both for systems with gasified components (Fig. 35) and for systems in which fuel is nonvolatile (Fig. 36);

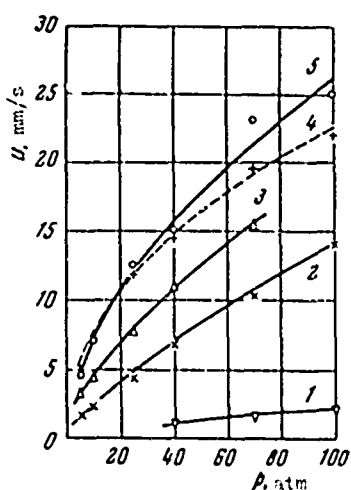


Fig. 35. Dependence $u(p)$ for a gelated mixture of NH_4ClO_4 (~40 microns) + polystyrene at different α [175]
 1 — $\alpha = 0.1$; 2 — $\alpha = 0.2$; 3 — $\alpha = 0.3$;
 4 — $\alpha = 0.5$; 5 — $\alpha = 1$.

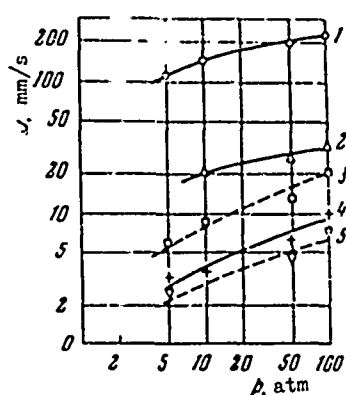


Fig. 36. Dependence $u(p)$ for a mixture of 10% $KClO_4$ + 90% W ($\alpha \approx 0.2$) at different dimension of tungsten particles [139].
1 - 2.7 microns; 2 - 19 microns;
3 - 160 microns; 4 - 340 microns;
5 - 550 microns.

II - to increase, approaching a certain constant value. This type of curve is usual enough for pyrotechnic mixtures (Fig. 37 and curves 2 and 4

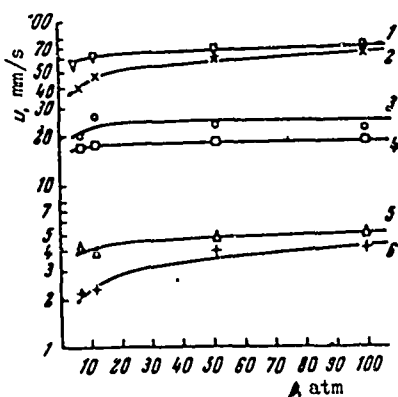


Fig. 37. Dependence $u(p)$ for a mixture of Al + Fe_2O_3 ($\alpha = 1$) at different dimension of aluminum particles and different diameter of charge [139].
1 - $d_{Al} \approx 0.1$ microns, $\phi 6.0$ mm;
2 - $d_{Al} \approx 3$ microns, $\phi 6.0$ mm;
3 - $d_{Al} \approx 12$ microns, $\phi 10.0$ mm;
4 - $d_{Al} \approx 12$ microns, $\phi 6.0$ mm;
5 - $d_{Al} = 170$ microns, $\phi 10.0$ mm;
6 - $d_{Al} = 540$ microns, $\phi 10.0$ mm.

on Fig. 38). However, it is sometimes also observed [103, 141, 175] for mixtures with organic fuels (Fig. 39);

III - to remain constant in the whole range of pressure studied (see curve 1 on Fig. 38). This type of curve is comparatively rare;

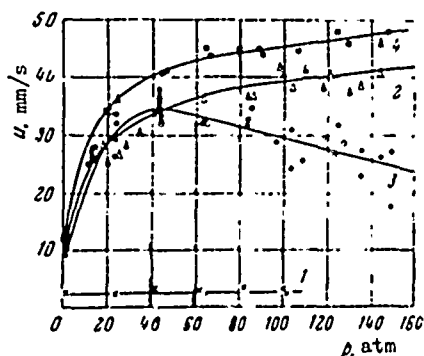


Fig. 38. Dependence $u(p)$ for series of thermites [157].

1 (x) - $Cr_2O_3 + 2 Al$; 2 (Δ, a) - $Fe_2O_3 + 2 Al$;
3 (O, o) - $Cr_2O_3 + 3 Mg$; 4 (m) - $3 MnO_2 + 4 Al$;
x, o, a, m - experiments in nitrogen;
O, Δ - experiments in argon.

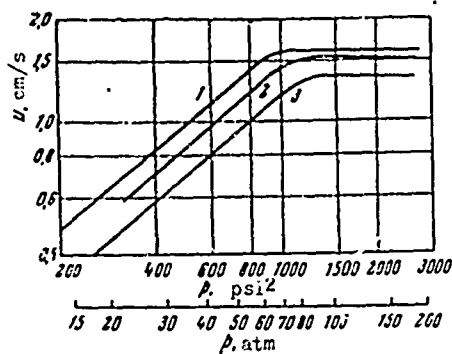


Fig. 39. Dependence $u(p)$ for mixtures of NH_4ClO_4 (76-104 microns) + para-formaldehyde (<76 microns) at different ratio between fuel and oxidizer [141]
1 - $\alpha = 2.23$; 2 - $\alpha = 1.0$; 3 - $\alpha = 0.64$.

IV - to increase, then to remain constant in a certain interval of pressure ("plateau"), and after that increase again (see curve 1 on Fig. 40). Curves

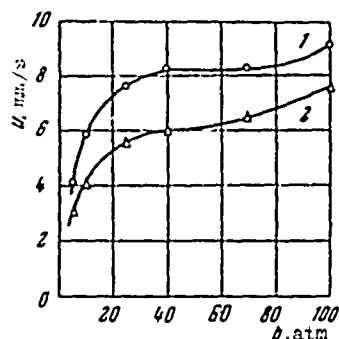


Fig. 40. Dependence $u(p)$ for gelated composition of NH_4ClO_4 + plexiglas ($\alpha = 0.7$) [168]. Fraction of NH_4ClO_4 : 1 - 80% (~5 microns) + 20% (140-320 microns); 2 - 50% (~5 microns) + 50% (140-320 microns).

of this type present considerable interest for solid fuels, but are encountered more rarely than curves of type I;

V - to increase up to a certain maximum, and then to decrease (sometimes up to damping of burning). This type of curve is observed (although rarely) both for mixtures with organic fuels (see curves 2 and 3 on Fig. 41), and for pyrotechnic mixtures (see curve 3 on Fig. 38).

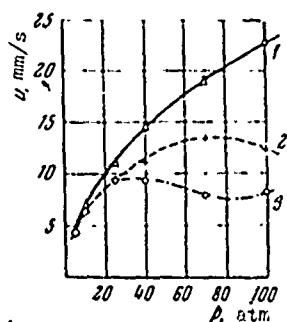


Fig. 41. Dependence $u(p)$ for a gelated mixture of NH_4ClO_4 (~5 microns) + plexiglas [175].
1 - $\alpha = 1$; 2 - $\alpha = 0.7$; 3 - $\alpha = 0.6$.

Of course there is no clear-cut line between the types of curves enumerated (especially between curves of type II and III; see Fig. 37). It is necessary to consider also that all experimental data pertain to a limited range of pressures. It is entirely possible that with expansion of this range a curve of type II is transformed to a curve of type IV, etc.

Factors determining form of dependence $u(p)$ have still been little investigated. Most natural explanation of rise in burning rate with increase of pressure (in those cases in which it occurs) consists in the fact that increase of pressure accelerates reaction in gas phase (just as in case of volatile VV and homogeneous gas mixtures).^{*} However, if for gas mixtures and volatile VV in a number of cases, it is possible to connect value of index ν in formula $m = bp^\nu$ and order of leading reaction $n = 2\nu$, then for condensed mixtures value ν is determined to a considerably lesser extent by order of reaction and depends on many other parameters (on degree of dispersion of components, their volatility, heat of their gasification, etc.). Absence of dependence of burning rate on pressure for nonvolatile VV is accepted in explanation of the fact that, in this case, the reaction in the condensed phase is the leading reaction.

Such an explanation is also possible for condensed mixtures (see [157, 250]). However, there is a number of examples (burning of mixtures with large surplus of organic fuel; burning of mixtures with polydispersional components; burning of certain layer systems) in which independence of burning rate from pressure is knowingly connected with other causes (see below).

Cases in which burning rate drops with rise in pressure can apparently, also be connected with different causes. Thus, in § 11 we examined the case in which decrease in burning rate with rise in pressure ($\nu < 0$) is connected with formation of crust of condensed residue on surface of charge (in the presence of leading reaction in gas phase). Systems with a large surplus of organic fuel for which on curves $u(p)$ there are also observed sections with $\nu < 0$, will be examined below.

B. Influence of Degree of Dispersion of Components on Dependence $u(p)$

From § 13 it is clear that degree of dispersion of fuel and oxidizer can essentially affect absolute value of burning rate. Experiments show that degree of dispersion of components also influences the form of curve $u(p)$.

For mixtures with organic fuel at a ratio of components not too far from stoichiometry, influence of degree of dispersion of components on form of curve $u(p)$ is comparatively weak. Dependence $u(p)$ is usually somewhat stronger for finely divided mixtures than for coarsely divided mixtures. Accordingly, value ν (in formula $u = bp^\nu$) decreases somewhat (or remains approximately constant) with increase of dimension of particles of components (Table 40).

For mixtures with a large surplus of organic fuel, dependence $\nu(d)$ is ambiguous: 1) for compositions 2-5 (see Table 40) value ν for finely divided

^{*}For condensed systems it is possible to construct theoretical models (see [202, 215] and others) within the bounds of which dependence $u(p)$ is connected with change of degree of dispersion during change of pressure (in the presence of a leading reaction in the condensed phase). This question has not yet been experimentally investigated.

Table 40. Influence of Degree of Dispersion of NH_4ClO_4 on Value v in formula $u = bp^v$ for Mixtures with Organic Fuels

Number of mixture	Fuel	d_{00}, μ	v							
			$\alpha = 2$	$\alpha = 1$	$\alpha = 0.7$	$\alpha = 0.5$	$\alpha = 0.3$	$\alpha = 0.2$		
1	Bitumen [173]	~ 15 ~ 120	0.61 0.55	0.59 0.53	0.53 0.48	0.52 0.51	—	—	—	—
2	Polystyrene ($< 100 \mu$) (non-related mixture) [175]	~ 6 ~ 40 $140-320$	— — —	0.50 0.50 0.51	0.50 — 0.52	0.55 0.44 0.47	— 0.58 0.49	0.91* 0.74 0.60	—	—
3	The same, related mixture [175]	~ 6 ~ 40 $140-320$	— — —	0.67 0.61 0.53	0.71 — 0.51	0.68 — 0.49	— 0.65 0.56	0.81 0.85 —	—	—
4	Polystyrene ($< 100 \mu$) (nonrelated mixture) [175]	~ 6 $63-100$ $100-140$ $320-463$	— — — —	0.53* 0.55* — 0.59*	— — — —	— — — —	— — — —	0.83 0.59* 0.59* —	—	—
5	Plexiglas ($\sim 3 \mu$) (nonrelated mixture) [170]	$63-100$ $100-140$	— —	— 0.33	0.36* ($\alpha = 0.6$) 0.36* ($\alpha = 0.6$)	0.69 ($\alpha = 0.4$) 0.41 ($\alpha = 0.4$)	— — —	1.08* — 0.83*	—	—
6	The same [175]	~ 6 $140-320$	0.44 0.45	0.36* 0.37	0.38* 0.41	— —	— —	— —	—	—
7	The same, gelated mixture [175]	~ 6 (5-25 atm) (25-40 atm) (40-100 atm) $140-320$ (5-25 atm) (25-100 atm)	0.53 0.53 0.53 0.66 0.48	0.55 0.55 0.52 0.42 0.56	0.50 0.36 —0.24 0.42 0.42	0.49 0.0 —0.15 0.43 0.54	— — — — —	— — — — —	—	—

*In 40-100 atm pressure range, in remaining cases (besides mixture 7) in 5-100 atm range.

res is considerably higher than for coarsely divided mixtures (i.e., essentially drops with rise in d); 2) for composition 7 the reverse effect is observed: value v for finely divided mixtures is much lower than for coarsely divided mixtures (at high pressures). Increase in v with decrease in d_{OK} is noted in work [146] for composition of 65% NH_4ClO_4 + 24% unsaturated polyester + 10% nitroglycerine:

d_{OK}, μ	40-53	53-74	74-88	88-105	105-117	117-207	207-500	500-710
v	0,33	0,33	0,36	0,37	0,37	0,36	0,42	0,45

Independence value of v from (or its weak dependence) on d_{OK} for compositions close to stoichiometrical compositions is more surprising than natural. It would be possible to expect that for finely divided mixtures, where influence of kinetic factors is greater, dependence $u(p)$ is stronger. As yet there is no satisfactory explanation why this has not been observed (or has almost not been observed) experimentally.

Conversely, the differences in value v for finely divided and coarsely divided mixtures with a large surplus of fuel are in many respects intelligible (see the following division).

It is necessary to stop separately on compositions with mixed (part coarsely divided + part finely divided) oxidizer (§ 13). In not all cases does burning rate of such mixtures monotonously grow with increase of pressure; furthermore, on curves $u(p)$ there are not infrequently sections where value v_{CM} is essentially higher or essentially lower than value v_M and v_{KP} , corresponding to compositions with finely divided and coarsely divided oxidizers. Thus, for example, in work [168] there is obtained for a gelated mixture of NH_4ClO_4 + polystyrene, $\alpha = 1$ (mixture I); for a nongelated mixture NH_4ClO_4 + polystyrene, $\alpha = 0.5$ (mixture II) and for a gelated mixture of NH_4ClO_4 + plexiglas, $\alpha = 1$ (mixture III) the following values v (near $p = 40$ atm):

	I	II	III
v_{KP}	0,55	0,47	0,41
v_{CM}	0,75	0,57	0,18
v_M	0,68	0,56	0,54

These results are connected with the fact that burning rate of compositions with mixed oxidizer u_{CM} is usually not the average of speeds of burning u_1 and u_{KP} for finely divided and coarsely divided compositions (see § 13). If at low pressures u_{CM} is close to u_{KP} and at high pressure is close to u_M , then obviously, $v_{CM} > v_M$ and $v_{CM} > v_{KP}$. Otherwise, v_{CM} will be below

than v_M and v_{kp} .

Up to now we have been examining mixtures with gasified components. For mixtures with nonvolatile fuels, judging by data of work [139], dependence $u(p)$ is stronger for coarsely divided mixtures and weaker for thinly divided mixtures (Table 41). For mixtures studied in work [139] ($KClO_4$ - W and

Table 41. Influence of Degree of Dispersion of Fuel on Value of Index v in Formula $u = bp^v$ for Mixtures of Oxidizer + Metal [139]

Mixture	α	v at dimension of particles of fuel, microns					
		0,1	2,7	19	160	350	550
20% $KClO_4$ + 80% W	$\sim 0,45$	—	0,21	—	—	0,53	—
10% $KClO_4$ + 90% W	$\sim 0,20$	—	0,23	0,20	0,42	0,40	0,37
5% $KClO_4$ + 95% W	$\sim 0,10$	—	0,20	—	—	0,33	—
75% Fe_2O_3 + 25% Al	~ 1	0,078	—	—	0,14	—	0,26

Fe_2O_3 - Al), this can be connected with regularities of transfer of oxidizer to surface of particles of fuel through layer of liquid residue (KCl , Fe and others) (see § 8B).

C. Influence of Fuel to Oxidizer Ratio on Dependence $u(p)$

The fuel to oxidizer ratio greatly influences dependence $u(p)$ (and, in particular, the value of index v in formula $u = bp^v$). For mixtures studied in work [175] (almost exclusively in region $0 < \alpha < 1$, i.e., during surplus of fuel), three types of curves $v(\alpha)$ were observed.

Type I. Value v rises with increase in surplus of fuel (i.e., with decrease in α). This type of curve $v(\alpha)$ is observed for very many mixtures (see compositions 2-5 in Table 40 and Fig. 42a). Curve $v(\alpha)$ for coarsely divided mixtures at

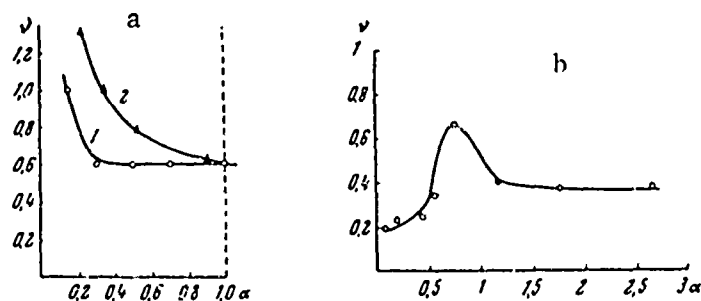


Fig. 42. Dependence $v(\alpha)$ (at $p = 5-100$ atm) a) is curve of type I [175]: 1 - NH_4ClO_4 (~40 microns) + polypropylene (<100 microns); 2 - $KClO_4$ (~10 microns) + urotropine (finely divided); b) is curve of type III [164]; (~10 microns) + tungsten (~3 microns).

all α goes essentially lower than for finely divided mixtures (see data for mixtures 2 and 4 in Table 40).

Type II. Value v drops with increase in fuel surplus. This type of curve was observed for a finely divided mixture of NH_4ClO_4 with plexiglas, especially at high pressures (see composition 7 in Table 40). An analogous effect was observed for finely divided mixtures of NH_4ClO_4 with polyformaldehyde (PFA) and urotropine. Thus, for example, in the 70-100 atm range, the following values for value v [175] are obtained:

α	v		α	v	
	ПФЛ	urotropine		ПФЛ	urotropine
1,0	0,53	0,72	0,50	0,0	—
0,75	0,57	—	0,25	—	0,0
0,65	—	0,80			

Type III. With decrease in α value v increases somewhat, passes through a maximum and starts to drop (Fig. 42b, for a mixture of KClO_4 - W). The maximum on curve $v(\alpha)$ is also obtained for a mixture of KClO_4 - graphite.

It is easy to understand that the question of how value v depends on α is connected with the question of how form of curve $u(\alpha)$ and position of maximum on curve $u(\alpha)$ depends on pressure:

1) if with increase in pressure the position of $u_{\max}$ and the form of curve $u(\alpha)$ remain constant (Fig. 43a), then index v , in general, does not depend on α ;

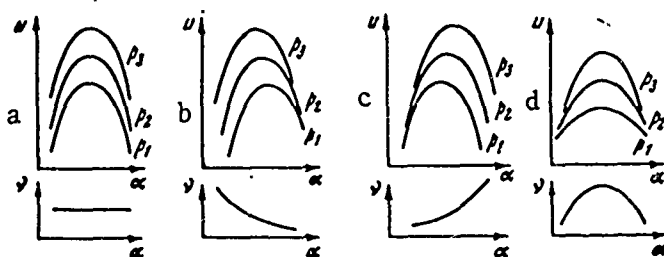


Fig. 43. Influence of position of maximum and form of curve $u(\alpha)$ at different pressures on character of dependence $v(\alpha)$.

2) if with increase in pressure $u_{\max}$ is displaced in the direction of surplus of fuel ($\alpha_{u_{\max}}$ decreases with rise in pressure) (Fig. 43b), then value v increases with increase in fuel surplus (curve $v(\alpha)$ type I);

3) on the contrary, if with increase of pressure $u_{\max}$ is displaced in the direction of stoichiometry or surplus of oxidizer (Fig. 43c), value v drops with decrease in α (curve $v(\alpha)$ type II);

4) if with increase in pressure curve $u(\alpha)$ becomes more and more steep (Fig. 43d), then value v has a maximum (curve $v(\alpha)$ type III).

In real conditions there can simultaneously change form of curve $u(\alpha)$ and position of $u_{\max}$. Let us give certain experimental data. In Table 42

Table 42. Lowering of Burning Rate with Increase in Fuel Surplus (as Compared to $\alpha_{u_{\max}}$ for Mixtures Based on NH_4ClO_4 at Different Pressures [175]

d_{acc}, μ	Fuel	d_{exp}, μ	$u/u_{\max}$	$u_{\max}$					
				1 atm	1.5 atm	2 atm	3 atm	5 atm	10 atm
~5 140- 320	Polystyrene	<100	0.4	0.52	0.58	0.61	0.65	0.72	0.81
	"	<100	0.4	0.59	0.69	0.78	0.81	0.84	0.93
~40 ~40	Polypropylene	<100	0.4	-	0.73	0.83	0.88	-	0.89
	Urotropine	Finely divided	0.4	0.46	0.46	-	0.54	-	0.62
~5	Plexiglas	Gelated mixture	0.7	-	-	-	-	0.71	0.55
~5 140- 320	"	The same	0.6	-	-	-	-	0.42	0.36
	"	"	0.4	-	0.61	0.75	0.75	-	-

the form of curve $u(\alpha)$ is characterized by value $u/u_{\max}$ at a given $\alpha/\alpha_{u_{\max}}$ (the more curve $u(\alpha)$ slope the closer $u/u_{\max}$ is to one).

For mixtures of NH_4ClO_4 with polystyrene, polypropylene, and urotropine, with rise in pressure, curve $u(\alpha)$ becomes more sloping ($u/u_{\max} \rightarrow 1$). Accordingly, in region of surplus of fuel, this leads to increase in v with decrease in α (curve $v(\alpha)$ type I).

Conversely, for gelated mixture of finely divided NH_4ClO_4 with plexiglas, curve $u(\alpha)$ becomes steeper with rise in pressure (i.e., $u/u_{\max}$ drops with rise in pressure). Accordingly, value v drops with increase in fuel surplus (curve $v(\alpha)$ type II).

In regard to shift in $u_{\max}$ with change in pressure, for nongelated mixture

H_4ClO_4 - polystyrene, and also mixtures of KClO_4 - dextrin and KClO_4 - urotropine, with rise in pressure, $u_{\max}$ is displaced in the direction of fuel surplus (accordingly, v increases at $\alpha \rightarrow 0$). Conversely, for gelated mixture of finely-dispersed NH_4ClO_4 with plexiglas, $u_{\max}$ is displaced in the direction of stoichiometry (from $\alpha \approx 0.8$ at $p = 5-40$ atm to $\alpha \approx 1$ at $p = 70-100$ atm). This promotes lowering of v at $\alpha \rightarrow 0$.

To clarify the meaning of dependence $v(\alpha)$ it is useful to examine also how surplus of fuel affects burning rate at low and high pressures. Let us assume that surplus of fuel is sufficiently great and knowingly lowers burning rate. If burning rate fall more strongly at low pressures and more weakly at high pressures, value v will increase at $\alpha \rightarrow 0$ (curve $v(\alpha)$ type I). This case corresponds to not too volatile (or to not very finely divided) fuel. At low pressures (when zone of influence is wide) surplus of such fuel is gasified completely or in considerable measure and strongly decreases burning rate. At high pressures (when zone of influence narrows) a smaller part of the excess fuel is gasified and burning rate decreases to a lesser extent.

Conversely, if properties of the fuel are such that its surplus lowers burning rate less at low pressures and more at high pressures, value v will fall at $\alpha \rightarrow 0$ (curve $v(\alpha)$ type II).

D. Influence of Initial Temperature and Nature of Components and Additions on Dependence $u(p)$

In literature there is only extremely scanty information concerning these questions.

The following consideration is evident: if with increase in T_0 or during introduction of this or that addition, burning rate increases more at high pressures and less at low pressures, dependence $u(p)$ is strengthened (v increases). In the opposite case (when burning rate increases more at low pressures and less at high pressures) dependence $u(p)$ is weakened (v decreases). For additions which lower burning rate, dependence $u(p)$ is strengthened (v increases) in those cases when addition is more influential at low pressures and less influential at high pressures.

In work [181] data are given on the influence of initial temperature on value v for a composition based on NH_4NO_3 (with addition $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ as catalyst). In this case value v is very slightly increased with rise in T_0 :

$T_0, ^\circ\text{C} \dots \dots$	-60	$-15,6$	$+76$
$v \dots \dots$	$0,184$	$0,333$	$0,416$

In work [185] for a composition of NH_4ClO_4 - polyurethane cluster - Al, it is shown that additions of copper chromite or SiO_2 considerably increases v (for initial composition $v \approx 0.11$; for composition with 1% SiO_2 $v \approx 0.31$, for composition with 1% chromite $v \approx 0.51$).

Especially strong influence of initial temperature and additions is observed in those cases in which on initial curve $u(p)$ there is a plateau (or, all the more so, a section where $v < 0$).

Thus, in work [216] burning is studied of a gelated mixture of NH_4ClO_4 (~5 microns) + plexiglas $\alpha = 0.5$. At 20°C on curve $u(p)$ for this mixture there is a maximum at $p \approx 20$ atm, and above 40 atm burning fades (Fig. 44). With

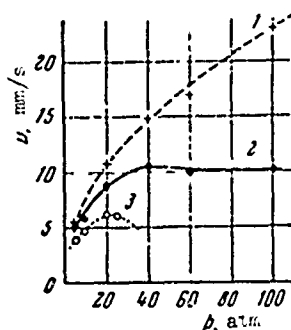


Fig. 44. Dependence $u(p)$ for a gelated mixture of NH_4ClO_4 (~5 microns) + plexiglas ($\alpha = 0.5$) at different initial temperature [216] 1 — +150°C; 2 — + 75°C; 3 — + 20°C.

increase in T_0 to 75°C, burning rate rises to ~40 atm and then remains practically constant (at least up to 100 atm). Finally, at 150°C burning rate monotonically increases with increase in pressure in the 5-100 atm range ($v_{5-100 \text{ atm}} \approx 0.52$).

In work [175] in gelated mixture of NH_4ClO_4 (~5 microns) + plexiglas $\alpha = 0.6$ (for which on curve $u(p)$ there is a maximum at ~25 atm) there was introduced an addition of less volatile fuel (polystyrene, charcoal) or catalytical addition (Cu_2O). In all these cases the form of curve $u(p)$ essentially changed (at 25-100 atm burning rate no longer decreased, but increased) (Fig. 45). An analogous result was obtained in work [141] during addition of soot to mixture of NH_4ClO_4 — paraformaldehyde.

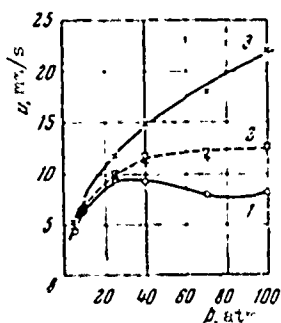


Fig. 45. Influence of additions on dependence $u(p)$ for a gelated mixture of NH_4ClO_4 (~5 microns) + plexiglas ($\alpha = 0.6$) [175]. 1 (○) — without additions; 2 (∇) — 2% polystyrene gelated together. Practically the same burning rate (+) is giving by a composition with 2% charcoal; 3 (x) — 2% Cu_2O .

Expounded results of works [185, 175, 141] will well agree with concepts (see § 8B) about simultaneous flow of homogeneous reaction (in mixture of products of gasification of NH_4ClO_4 and basic fuel) and heterogeneous reaction to particles of addition (gasification of polystyrene is accompanied by formation of particles of soot).

Nature of components can render strong influence on burning rate and form of dependence $u(p)$. However, up to now it remains vague to what extent this is connected with thermodynamic parameters of a given component (heat of gasification heat capacity, temperature transfer, enthalpy) and to what extent this is connected with the chemical structure of the substance examined. Specially these questions almost were not investigated.

Let us note only that compositions bases on $KClO_4$ differ by stronger dependence $u(p)$ than compositions based on NH_4ClO_4 . Thus, during the carrying out of work [173], it is shown that for compositions of oxidizer — bitumen ($\alpha = 0.75$), value v is 0.51-0.55 for NH_4ClO_4 and ~ 0.78 for $KClO_4$.

E. Dependence $u(p)$ at $p \leq 1$ [atm(abs.)]

Experimental data pertaining to the $p \leq 1$ [atm(abs.)] range are not very numerous and pertain only to mixtures of oxidizers with organic fuels (for pyrotechnic mixtures there are practically no data on dependence $u(p)$, although this pressure range is operational for them).

For oxidizer — organic fuel systems at low pressures, dependence $u(p)$ is essentially strengthened (as compared to "average" pressures).

For a number of such systems, dependence $u(p)$ at $p \leq 1$ [atm(abs.)] is close to $u = bp$ (see Table 43, and also Fig. 46).*

Table 43. Value of Coefficients v and b in
Formula $u = bp^v$ for Certain Mixture Systems at
Pressures Close to Atmospheric Pressure

Oxidizer	d_{OK}, μ	Fuel	α	v	$b, \frac{mm}{s \cdot atm}$	Pressure range atm	Literature
NH_4ClO_4	10—20	Trotyl	1	1,0	0,78	0,5—3,0	[195]
		Bitumen	1	1,0	1,4	0,2—1,0	[195]
	200	"	1	$\sim 0,7$	$\sim 0,9$	0,3—1,0	[195]
$KClO_4$	10—20	"	1	1,0	0,76	0,2—1,0	[195]
NH_4ClO_4	76—104	Para-formaldehyde	1	1,0	0,7	0,1—1,0	[103]
	—	The same	2,8	1,0	0,7	0,1—1,0	[109]
	—	Polystyrene — polyester cluster (20%)	—	1,0	1,02	0,2—1,0	[193]

*Let us remember that dependence $u = bp$ is characteristic for volatile VV (see Table 16).

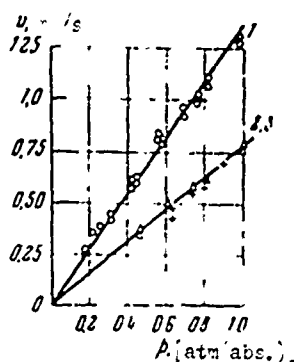


Fig. 46. Dependence of burning rate of finely divided mixtures on pressure at $p \leq 1$ [atm(abs.)] [195]. 1(○) — NH_4ClO_4 + bitumen ($\alpha = 1$); 2(Δ) — NH_4ClO_4 + trotyl ($\alpha = 1$); 3(+) — KClO_4 + trotyl ($\alpha = 1$).

Dependence $u = bp$ (at $p \leq 1$ [atm(abs.)]) for a series of compositions with gasified components is obtained also in work [197].

Increase of index v with decrease in pressure is noted (for system with gasified components) and in work [151]; however, v increases not to one, but to $v = 0.70$ - 0.75 (Table 44).

Table 44. Value of Index v (in Formula $u = bp^v$) at Different Pressures for NH_4ClO_4 — Polyester Composition [151]

NH ₄ ClO ₄ polyester	p, atm	v							
		0.2 [atm(abs.)]	0.4 [atm(abs.)]	0.7 [atm(abs.)]	1.0 [atm(abs.)]	2.0 [atm(abs.)]	5.0 [atm(abs.)]	7.0 [atm(abs.)]	10 [atm(abs.)]
75/25	40,6	0,7	0,7	0,69	0,68	0,67	0,60	0,48	0,40
70/30	40,6	0,7	0,7	0,66	0,64	0,63	0,47	0,43	0,42
75/25	75	0,72	0,67	0,65	0,64	0,64	0,59	0,51	0,47
70/30	75	0,75	0,68	0,66	0,66	0,66	0,54	0,47	0,27
70/30	120	0,7	0,7	0,69	0,68	0,64	0,58	0,56	0,56

The point of view is natural (expressed in works [195, 197]), according to which strong dependence $u(p)$ for systems with gasified components at low pressures is connected with the fact that in these conditions mixing of components can be completed in zone of heating, and burning goes on in kinetic conditions (§ 8A), analogous to burning of homogeneous volatile VV. From § 2B it is clear that in this case $v \approx 1$.

However, consent of this point of view with experiment is not exhaustive. First of all there will not be in agreement with ideas about complete mixing of components (in zone of heating) the fact that during burning in vacuum, combustion efficiency decreases and probability of dispersion increases. In particular, in work [98] it is shown that for stoichiometrical mixtures of KClO_4 + Zr and KClO_4 + W at $p \approx 10^{-2}$ mm of mercury, completeness of burning of metal is ~7%, for Zr and ~12% for W.

Besides this, from the stated point of view the following regularity would have to be observed: the greater the dimension of particles of components, the lower the pressure (more exactly, the lower the burning rate), starting from which dependence $u(p)$ becomes strong. However, during experiment no such regularity is observed (see Table 44).

F. Dependence $u(p)$ at Pressures in Hundreds and Thousands of Atmospheres

Dependence $u(p)$ in this pressure range is studied only in work [42] (in a constant pressure bomb at $p \leq 1000$ atm) and in work [44] (in a variable pressure bomb at $p \leq 4000$ atm). According to these works, dependence $u(p)$ in region of high pressures can be essentially different than $p \leq 100-200$ atm (Fig. 47):

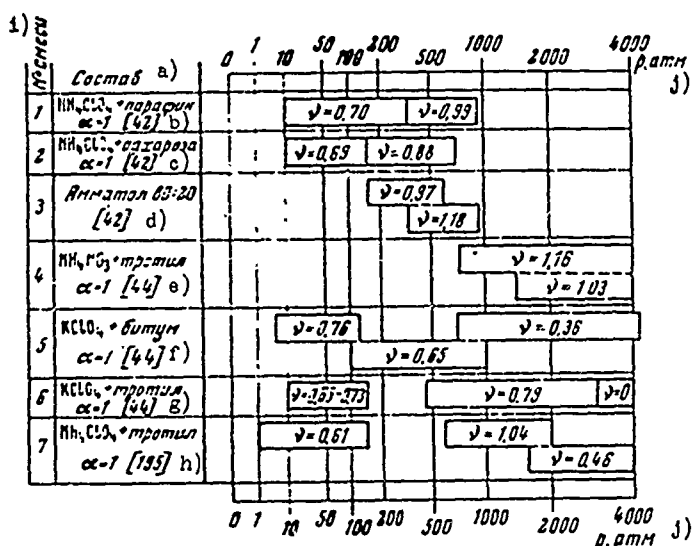


Fig. 47. The value of index v in formula $u = bp^v$ for a number of condensed mixtures in different pressure ranges.
KEY: a) Composition; b) NH_4ClO_4 + parafin; $\alpha = 1$ [42]; c) NH_4ClO_4 + oakharoza [no translation found] $\alpha = 1$ [42]; d) Ammatol [no translation found] 80:20 [42]; e) NH_4NO_3 + trotyl $\alpha = 1$ [44]; f) KClO_4 + bitumen $\alpha = 1$ [44]; g) KClO_4 + trotyl $\alpha = 1$ [44]; h) NH_4ClO_4 + bitumen $\alpha = 1$ [195]; i) Mixture No; j) atm.

a) for mixtures 1, 2, 7 (Fig. 47) dependence $u(p)$ in the interval $p \approx 300-1000$ atm is noticeably strengthened as compared to the interval $p \leq 100-200$ atm;

b) for mixtures 1, 2, 3, 7 (in the interval ~200-1000 atm), and also for mixture 4 (in the interval 1000-4000 atm), dependence $u(p)$ is close to a direct ratio;

c) for mixtures 5, 7 and especially 6 at sufficiently high pressures, dependence $u(p)$ is essentially weakened.

For mixture 7 it is possible to trace the form of dependence $u(p)$ in a very wide pressure range: from ~0.5 [atm(abs.)] to 4000 atm (Fig. 48).

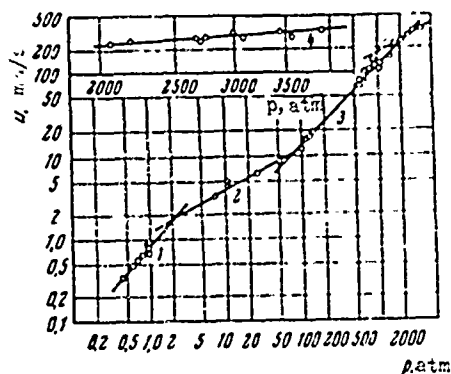


Fig. 48. Dependence $u(p)$ for mixture of finely pulverized NH_4ClO_4 and trotyl ($\alpha = 1$) [195]. Data in interval 2000-4000 atm (straight line 4) are given above on a larger scale (along the p axis).

In this case on curve $u(p)$ there are four different sections; at "low" (< 1 [atm(abs.)]; § 1) and "high" (600-2000 atm; § 3) pressures, dependence $u(p)$ is linear,* but at "average" § 2) and "superhigh" § 2) and "superhigh" § 4) pressures, it is considerably weaker. Certainly, experimental data available at "high" and "superhigh" pressures are very scanty up to now, but are nonetheless, of great theoretical interest.

Weakening of dependence $u(p)$ is more understandable at sufficiently high pressures. Actually, rise in burning rate with increase in pressure is connected with increase of speed of reaction in kinetic zone near "spouts" of flame (see § 9, 10). Accordingly, with increase of pressure, zone of reaction ever nearer approaches summit "of spout," (what leads to increase of withdrawal of components which reacts outside zone of influence). From this point of view, at sufficiently high pressures, dependence $u(p)$ should be weakened.

Of course, such qualitative considerations and such a scanty experiment are still insufficient to prove that weakening of dependence $u(p)$ by virtue of the examined mechanism will be observed exactly at several thousands of atmospheres.

The reason are less clear why for a number of mixtures (but not for all

*The slope of straight line $u(p)$ at "low" pressures is considerably greater than "high" pressures (value b in formula $u = bp^{-0.78}$ (mm/s)/atm at "low" pressures and ~0.115 (mm/s)/atm at "high" pressures.

mixtures), dependence $u(p)$ is strengthened during transition from "average" pressures to "high" pressures.*

§ 16. Dependence of Burning Rate on Initial Temperature

With increase of initial temperature T_0 , burning rate of condensed mixtures (as well as burning rate of homogeneous gas mixtures (see § 1D) and volatile VV (see § 2B) monotonously increases. Consequently, the form of curve $u(T_0)$ is simpler than the form of curves $u(p)$ or $u(d)$.

In order to characterize dependence $u(T_0)$, we will use (just as in § 1D and § 2C) temperature coefficient

$$\beta = \frac{1}{u} \frac{du}{dT_0} = \frac{d \ln u}{dT_0} \approx \frac{d \ln m}{dT_0} \text{ deg}^{-1}.$$

Obviously, if with increase of T_0 by 1° , burning rate increases 1%, then $\beta = 10^{-2} \text{ deg}^{-1}$ etc. If in a certain range, $T_{02} - T_{01}$ experimental points at coordinates $\ln u$, T_0 are grouped with satisfactory accuracy around a certain straight line, then in this range $\beta = \text{const} = \text{tg } \phi \approx (\ln u_2/u_1)/(T_{02} - T_{01})$, where ϕ is angle of inclination of the given straight line to axis T_0 . If range T_0 is too wide, it can be split into several sections and value β can be found for every section separately.

In § 1D we noted that for gas mixtures value β drops with rise in T_0 . Conversely, for nitroglycerine powder (see § 5) there was observed increase in β with rise in T_0 (especially in the $0-40^\circ\text{C}$ range). For condensed mixtures it is frequently possible to take $\beta \approx \text{const}$ (Fig. 49) in a sufficiently wide

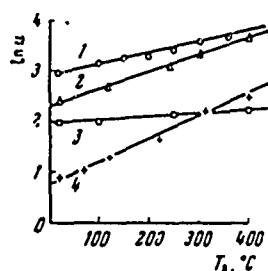


Fig. 49. Dependence of burning rate on initial temperature for thermite compositions [165].
 1 — Al — Fe_2O_3 ($\alpha = 1$); 2 — B — Fe_2O_3 ($\alpha = 1$);
 3 — Mg — Fe_2O_3 ($\alpha = 1$); 4 — W — KClO_4 ($\alpha = 1.78$).

*Only the case of mixtures of type NH_4ClO_4 (or NH_4NO_3) — trotyl seems comparatively simple, where both components are capable of independent burning, where for each of them dependence $u(p)$ is close to linear (in region of high pressures).

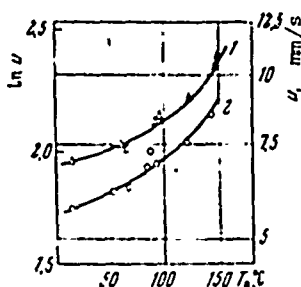


Fig. 50. Dependence of burning rate on initial temperature for a nongelated mixture of NH_4ClO_4 + polystyrene ($\alpha = 1.5$) [216].

1 - $d_{OK} \approx 10$ microns; 2 - $d_{OK} = 140-320$ microns.

range T_0 . However, for certain mixtures β distinctly increases with increase in T_0 (see Fig. 50 and Table 45).

Table 45. Dependence $u(T_0)$ for Composition of NH_4NO_3 + Organic Cluster [181]

$\Delta T_0, ^\circ\text{C}$	$\beta \cdot 10^3 \text{ deg}^{-1}$				
	$p = 28 \text{ atm}$	$p = 32 \text{ atm}$	$p = 56 \text{ atm}$	$p = 70 \text{ atm}$	$p = 100 \text{ atm}$
$-60 \div -15,6$	2,53	2,47	2,52	2,44	2,41
$15,6 \div 76$	3,0	3,01	3,35	3,73	3,73

Note. There was investigated a composition of 72.79% NH_4NO_3 , 9.79% polyester rubber (Genpol A-20), 12.22% of methylacrylate, 2.22% styrene, 1.99% $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ and ~1% technological additions. Value β is calculated by us according to experimental points $u(T_0)$.

Temperature coefficient can also depend on pressure. In Chapter I we showed that for volatile VV (and also for nitroglycerine powder) there is observed essential decrease in β with rise in pressure (thus, for example, for nitroglycerine powder [45] with increase in pressure from 10 to 50 atm, value β decreases three times, from $12 \cdot 10^{-3}$ to $4 \cdot 10^{-3} \text{ deg}^{-1}$). For condensed mixtures dependence $\beta(p)$ is investigated for only a few mixtures. β usually drops weakly with rise in pressure. Thus, for example, for a mixture of NH_4ClO_4 (~10 microns) + bitumen $\alpha = 1$, there is obtained [45]:

$$\beta_{1 \text{ atm}} = 1,7 \cdot 10^{-3} \text{ deg}^{-1}, \beta_{50 \text{ atm}} = 1,4 \cdot 10^{-3} \text{ deg}^{-1}$$

(in the $+20$ – $+90^\circ\text{C}$ range). In certain cases fall in β with rise in pressure is considerable (see mixture 1.2 Table 46).

However, cases are also possible in which temperature coefficient increases with increase in pressure (see mixture 3 Table 46, and also dependence $\beta(p)$ in the $15,6$ – 76°C range in Table 45).

Table 46. Value of β for a Number of Mixtures at Different Pressures [165]

No. n.n.	Mixture	$\beta \cdot 10^3, \text{deg}^{-1}$			
		1 [atm(abs.)]	5 atm	10 atm	20 atm
1	$\text{KClO}_4 (\sim 10 \mu) +$ $+ \text{W} (\sim 3 \mu)$ $\alpha = 1.78$	4.43 (20—40)*	3.4 (20—20)*	2.5 (20—20)*	2.3 (20—20)*
2	85% KNO_3 + 15% charcoal	5.0 (20—30)*	—	3.1 (20—250)*	—
3	Smoky powder ДРП-3	1.4 (50—30)*	—	2.8 (20—225)*	—

Note. Data, taken in parentheses, — interval of ΔT_0 in $^{\circ}\text{C}$.

The presence of dependence of temperature coefficient on initial temperature and pressure, of course, hampers comparison of values β for different systems, since experimental data frequently pertain to different ranges of initial temperatures and different pressures. Fortunately for systems with organic fuels, dependence $\beta(p)$ at $p > 1$ [atm(abs.)] is weak (according to certain data at $p < 1$ [atm(abs.)] value β can essentially increase with decrease in pressure).

A. Order of Magnitude of Temperature Coefficient β

Above we showed that at atmospheric pressure for homogeneous mixtures of combustible gases with air, value β usually lies within limits $(1-2) \cdot 10^{-3} \text{deg}^{-1}$ (see Table 9), for volatile VV — within limits $(3-7) \cdot 10^{-3} \text{deg}^{-1}$ (see Table 17), for nitroglycerine powder — within limits $(2-16) \cdot 10^{-3} \text{deg}^{-1}$ (depending upon interval T_0).

For condensed mixtures order of magnitude* of β is also 10^{-3}deg^{-1} .

For mixtures with organic fuels in a composition not too far from stoichiometry, value β for finely divided mixtures usually lies within limits $(1-2) \cdot 10^{-3} \text{deg}^{-1}$, and for coarsely divided mixtures within limits $(2-3) \cdot 10^{-3} \text{deg}^{-1}$.

*Measurement of temperature coefficient for condensed mixtures (especially coarsely divided mixtures because of its small value involves great methodical difficulties. Actually, in order to measure value of temperature coefficient close to $1 \cdot 10^{-3} \text{deg}^{-1}$, with a precision of 20%, it is necessary to measure burning rate, for example, at temperatures of T_{01} and $T_{02} = T_{01} + 100^{\circ}$ with a precision of ~1%, which lies at the limit of accuracy of existing methods of burning rate measurement.

Thus, temperature coefficient for mixtures with organic fuels lies in the same limits as temperature coefficient for gas mixtures (and is considerably lower than temperature coefficient for ballastite powders). Only at very great surplus of fuel does value β for mixture systems sharply increase (up to $3 \cdot 10^{-3} - 7 \cdot 10^{-3} \text{ deg}^{-1}$; see below).

For mixtures with metals and charcoal (not too distant from stoichiometry), value β lies within limits $(0.5-5) \cdot 10^{-3} \text{ deg}^{-1}$. Let us note that in work [165] an assumption is expressed according to which value β increases with increase in boiling point of metal. Thus, for stoichiometrical mixtures based on Fe_2O_3 there is obtained (in the $20-400^\circ\text{C}$ range):

Metal, ...	Mg	Al	B
B.P. of metal, $^\circ\text{C}$	1100	~ 2300	~ 2500
$\beta \cdot 10^3, \text{ deg}^{-1}$	0.7	2.2	3.4

We will examine data for black powder in § 20.

B. Influence of Fuel to Oxidizer Ratio on Value β

This question is studied in comparative detail only for mixtures with organic fuels.

A distinct regularity was established [216]: curve $\beta(\alpha)$ has a minimum, the position of which approximately coincides with the position of maximum burning rate (see Tables 47 and 48 and Fig. 51). On both sides of minimum, temperature coefficient essentially increases.

Table 47. Dependence $\beta(\alpha)$ for Mixture of NH_4ClO_4 + Polystyrene [216] $p = 40 \text{ atm}$, $\Delta T_0 = 15-140^\circ\text{C}$

d_{gr}, μ	d_{gr}, μ		α							
			2.0	1.5	1.0	0.63	0.5	0.3	0.2	
~ 10	related mixture	$\beta \cdot 10^3, \text{ deg}^{-1}$	4.2	4.4	2.0	2.0	1.3*	3.0	8.3	
		$u_{15^\circ\text{C}}, \text{ mm/s}$	10.5	13.5	20.2	23.8	25.5	16.7	5.3	
	< 10	$\beta \cdot 10^3, \text{ deg}^{-1}$	3.5	4.4	1.8	—	1.2	—	3.4	
		$u_{15^\circ\text{C}}, \text{ mm/s}$	—	6.9	9.0	—	11.6	—	7.5	
$150-320$	< 10	$\beta \cdot 10^3, \text{ deg}^{-1}$	2.6	3.2	2.6	—	1.8	—	4.1	
		$u_{15^\circ\text{C}}, \text{ mm/s}$	5.6	5.8	6.3	—	6.5	—	4.9	

*See note to Table 37.

Table 48. Temperature Coefficient for Composition NH_4ClO_4 + Polyester Cluster $p = 1$ [atm(abs.)]
[151]

d_{0K}, μ		% oxidizer % cluster			
		80/20	75/25	70/30	65/35
~40	$\beta \cdot 10^3, \text{deg}^{-1}$	1,2 (27—147° C)	1,8 (27—157° C)	1,5 (27—167° C)	2,3 (97—167° C)
	$u_{20}, \text{C}, \text{mm/s}$	1,1	1,03	0,98	0,76
75	$\beta \cdot 10^3, \text{deg}^{-1}$	1,7 (27—177° C)	1,7 (37—167° C)	2,0 (37—207° C)	2,7 (77—187° C)
	$u_{20}, \text{C}, \text{mm/s}$	1,05	0,94	0,85	0,64

Note. If elemental composition of cluster is close to $\text{C}_2\text{H}_4\text{O}$, then to oxidizer to fuel ratio 80/20, 75/25, 70/30, 65/35, there corresponds value $\alpha \approx 0.76, 0.56, 0.44$ and 0.35 .

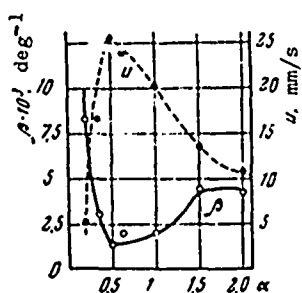


Fig. 51. Dependence of temperature coefficient β and burning rate u on fuel to oxidizer ratio for a gelled mixture of NH_4ClO_4 (~10 microns) + polystyrene: $p = 40$ atm [216].

C. Influence of Degree of Dispersion of Components on Value β

For mixture with organic fuel at a ratio of components close to the stoichiometrical ratio, temperature coefficient increases with increase of dimension of particles of oxidizer (Table 49).

Table 49. Dependence $\beta(d_{OK})$ for a Number of Stoichiometrical Mixtures [216]

Mixture	d_{OK}, μ	$\beta \cdot 10^3, 1/\text{deg}$	$T, ^\circ\text{C}$	p, atm
NH_4ClO_4 - bitumen.	~ 10 ~ 1800	1,4 2,6	20-90 15-100	22,5
KClO_4 - bitumen.	~ 10 ~ 1800	1,4 5,0	20-90 20-90	
NH_4ClO_4 - polystyrene (<100 μ) (nongelated mixture)	~ 10 100-320	1,8 2,6	15-135 15-135	40
NH_4ClO_4 - plexiglas (gelated mixture)	~ 5 100-150	1,2 2,6	15-170 15-180	10

Conversely, with sufficient surplus of fuel or oxidizer, values β_M and β_{HP} can approach and, moreover, β_M can exceed β_{HP} . Thus, for a nongelated mixture of NH_4ClO_4 - polystyrene (<100 microns) there is obtained (see Table 47):

α	2	1,5	1,0	0,5	0,2
β_{HP}/β_M	0,74	0,73	1,45	1,50	1,20

An analogous conclusion follows from the data of Table 48.

Regarding mixtures with nonvolatile fuels, in work [165] for mixture $W + \text{KClO}_4$ ($\alpha = 0.76$) at 1 [atm(abs.)] there revealed no dependence β on dimension of particles of tungsten (at $d_W \approx 3, 40-100$ and $140-400$ microns, value β in the $20-200^\circ\text{C}$ range remained, within limits of scattering, constant and equal to $\sim 3.1 \cdot 10^{-3} \text{ deg}^{-1}$).

* * *

In conclusion of this paragraph, we will pause to the experimental data which have been stated.

The basic idea here is that magnitude of temperature coefficient β is determined by temperature $T_{3\phi\phi} = T_F$ in zone of leading reaction: if T_F

is great, β ; conversely, if T_p is small, β is great [45, 47]. This circumstance is also reflected in formula (7) $\beta = E/2RT_p^2$.

For coarsely divided mixtures, the composition of which not too far from stoichiometry, an essential part of the heat emanated in the zone of influence is expended heating particles which react far from the zone of influence. Therefore, for coarsely divided mixtures as compared to finely divided mixtures, value T_p is lower and temperature coefficient is higher, respectively.

However, with increase in surplus of one of the components, the difference between values of T_p for coarsely divided and finely divided mixtures is smoothed, since in zone of influence for a coarsely divided mixture, a smaller part of the excess component is gasified than for a finely divided mixture. Accordingly, values β_{kp} and β_M converge (and with a sufficient surplus of one of the components, the case is possible in which $\beta_{kp} < \beta_M$).

We will now examine dependence $\beta(\alpha)$. Maximum equilibrium combustion temperature T_p lies near $\alpha = 1$ (a certain deviation from $\alpha = 1$ can be connected with dissociation of combustion products). For finely divided mixtures with volatile components, value T_p is close to T_p . Therefore, $u_{\max} = f[(T_p)_{\max}]$, $\beta_{\min}$ and $(T_p)_{\max}$ coincide and lie near $\alpha = 1$ (see Fig. 52 for a finely divided NH_4ClO_4 - polyformaldehyde mixture).

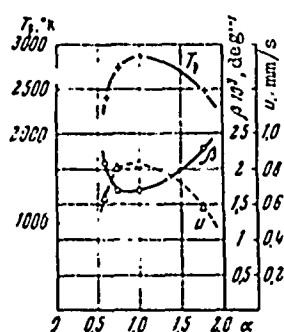


Fig. 52. Dependence of temperature coefficient β , burning rate u and equilibrium combustion temperature T_p (calculation) on the fuel to oxidizer ratio for a finely divided NH_4ClO_4 - polyformaldehyde mixture at atmospheric pressure.

However, in the case of NH_4ClO_4 - polystyrene mixtures, gasification of fuel will lag behind gasification of oxidizer and is accompanied by formation of soot. Burning of particles of soot takes place comparatively slowly and is not completed within the limits of the zone of influence. In order that mixture reacting in zone of influence not contain surplus of oxidizer, it is necessary to create sufficient surplus of fuel in the initial mixture. Therefore, for NH_4ClO_4 - polystyrene mixture, $u_{\max} = f[(T_p)_{\max}]$ and $\beta_{\min}$ lie at a considerable surplus of fuel ($\alpha \approx 0.5$) and do not coincide with $(T_p)_{\max}$.

Weak dependence of temperature coefficient on pressure (at $p > 1$ [atm(abs.)]) indicates apparently, that fullness of burning is already attained for mixture systems at low pressures, and further rise in pressure has little effect on

due to T_F . However, there are also cases in which β increases with increase in pressure. Of this case the case shown on Fig. 44 is sufficiently understandable, in which ordinary temperature, burning rate drops with rise in pressure (due to lowering of T_F , combined with change in unfavorable side of ratio of components in zone of influence; with increase of role of thermal losses, etc.). Obviously, in this case β will increase with pressure increase.

§ 17. Influence of Catalytical Additions

Thus, as in the case of gas mixtures, burning rate of condensed mixtures can be changed with the help of small (not more than several percents) additions.

Inasmuch as the action of such additions on burning rate in most cases is knowingly not explained by their influence on heat of burning (many additions which increase burning rate only lower heat of burning), it has been agreed to call them catalytical additions. However, it is not clear whether they are catalysts in the exact sense of the word.

Data available in literature (extremely scanty) show that with the help of catalytical additions, it is possible to change burning rate of condensed mixtures not more than 2-3 times. This is essentially less than for gas mixtures, for which by introducing 1-2% additions, it is possible to change burning rate up to 5-10 times (see Tables 10, 11).

Thus, the action of catalytical additions on burning rate is immeasurably weaker than the action of catalysts on speed of chemical reactions at low and moderate temperatures (when additions can change burning rate many orders and tens of orders of magnitudes). This circumstance is connected with the very general principle, according to which to affect speed of reaction is the more difficult, the higher the temperature at which it takes place.

Nonetheless, catalytical additions can play a very important role in burning, and systems based on NH_4NO_3 , in general, are not used without catalysts because of insufficient stability of burning. Let us also note that at ordinary temperature pure NH_4ClO_4 and NH_4NO_3 can burn only at sufficiently high pressure (NH_4ClO_4 at $p \geq 30-40$ atm, NH_4NO_3 — at considerably higher pressure).^{*} Catalytical additions permit carrying out burning of NH_4ClO_4 and NH_4NO_3 even at atmospheric pressure.

Let us first consider data available in literature on catalytical additions to systems based on NH_4NO_3 . In most cases 2-3% bichromate of ammonium $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ [180, 181] is used as catalyst. According to [182], K_2CrO_4 and $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$.

^{*}According to work [237], NH_4NO_3 burns in a manometric bomb at $p \geq 130$ atm. In a bomb of constant pressure, it was not possible to carry out stable burning of NH_4NO_3 at $p \leq 1000$ atm.

Table 50. Burning Rate of Mixture of NH_4NO_3 + 10% Additions at Atmospheric Pressure [183]

Addition	relative density of charge δ	u , mm/s	w , g/cm ² ·s
K_2CrO_4	0,5	1,73	0,084
$\text{K}_2\text{Cr}_2\text{O}_7$	0,5	1,33	0,063
$\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$	0,6	0,83	0,04
$(\text{NH}_4)_2\text{Cr}_2\text{O}_7$	0,5	0,32	0,015
$(\text{NH}_4)_2\text{CrO}_4$	0,5	0,23	0,012

are the most effective catalysts. High effectiveness of K_2CrO_4 is also confirmed in work [183]; however, according to this work, $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ is considerably less effective (Table 50) (one should consider that work [183] was conducted at 1 [atm(abs.)], whereas works [180, 181] pertain to 30-300 atm pressure). In work [108, 180] the action of Cr_2O_3 is also studied; however, it is revealed that $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ acts more strongly than an equivalent concentration of Cr_2O_3 .

It is necessary to note that appraisal of effectiveness of additions is hampered by the fact that in works [108, 180-183] burning rate is not given of the same systems not containing additions (at low pressures such data cannot be obtained, since mixtures based on NH_4NO_3 , not to mention pure NH_4NO_3 , do not burn in this case).

An exception in this respect is the data of work [184] on influence of additions of certain surface-active substances on burning rate of composition based on NH_4NO_3 . Thus, for example, for sodium dinaphthylmelhanedisulphonate there is obtained:

Addition %	0	0,1	1,0	2,0	3,0
u_p = 1 atm, mm/s	0,97	1,17	1,50	1,58	1,57
$Z = \frac{u_{\text{с добавкой}}}{u_{\text{без добавки}}}$	—	1,20	1,55	1,63	1,62

As additions increasing burning rate of NH_4ClO_4 and of compositions based on it, there was used CuO [120], copper chromite (85% CuO + 15% Cr_2O_3) [120, 185, 187], Cu_2O [173, 175], Fe_2O_3 [120], SiO_2 [185], Cu_2Cl_2 [186] and others, and as additions lowering burning rate, — LiF [185, 187].

For NH_4ClO_4 — fuel mixtures with the help of 1-2% additions, it was possible to change burning rate not more than 1.5-2 times. Pure NH_4ClO_4 to a larger

degree yields to the action of additions: at 2-5% additions it is possible to change its burning rate up to 3-4 times.

Data given in the works enumerated permit reaching certain conclusions about regularities of action of catalytical additions.

1. The action of additions is strengthened during crushing of oxidizer. Thus, in work [187] there was studied a composition of 76% NH_4ClO_4 + 24% cluster at $d_{\text{OK}} \approx 15$ and ~ 80 microns (at $p = 14$ atm burning rate equaled 8.4 and ~ 4.2 mm/s respectively). Addition of 1% copper chromite increased burning rate (at 14 atm) of finely divided compositions 1.67 times and of coarsely divided composition 1.58 times. Addition of 1% lithium fluoride lowered burning rate of finely divided composition 1.7 times, and of coarsely divided composition only 1.23 times.

2. The action of addition is strengthened with increase in percentage of addition (within limits up to 2-5%). Thus, for example, in work [185] for composition of 70% NH_4ClO_4 + 25% polyesterurethane cluster + 5% Al there is obtained:

LiF, %	0	0,5	1,0	1,5	2,0
$u_{\text{burn}}, \text{ m/s}$	5,8	5,17	4,52	3,92	3,23
Z	—	0,89	0,78	0,68	0,57

Analogous results for addition of copper chromite are given in work [120] (Table 51) and in work [187] (Table 52).

Table 51. Influence of Pressure on Effectiveness of Action of Additions on Burning Rate of Pure NH_4ClO_4 [120]

Addition		Pressure, atm							
		5	6	7	8	9	10	11	12
without addition	$u, \text{ mm/s}$	6,3	7,2	8,2	8,9	9,5	10,2	11,3	12,3
	$u, \text{ mm/s}$	11,1	17,1	23,2	27,4	30,7	33,6	36,6	41,6
3% copper chromite	Z	1,7	2,36	2,83	3,08	3,23	3,39	3,55	3,71
	$u, \text{ mm/s}$	22,2	26,1	30	32,8	35,2	38	40,8	43,6
5% copper chromite	Z	3,52	3,6	3,66	3,68	3,71	3,73	3,81	3,84
	$u, \text{ mm/s}$	22,2	26,1	30	32,8	35,2	38	40,8	43,6

Note. Numerical data are taken from graphs.

Table 52. Influence of Pressure on Effectiveness of Action of Additions on Burning Rate of Composition of NH_4ClO_4 - polyurethane cluster - Al [185]

Addition		Pressure, atm			
		6	5	4	3
Without addition	u , mm/s	5.14	5.19	5.26	5.34
1% copper chromite	u , mm/s	6.49	6.86	7.32	7.75
	Z	1.26	1.32	1.39	1.45
1% SiO_2	u , mm/s	8.35	8.72	9.0	9.3
	Z	1.62	1.68	1.71	1.74

Note. Numerical data are taken from graphs.

3. Effectiveness of action of additions depends on pressure. For copper chromite and silicon oxide, the addition acts more strongly the higher the pressure (see Table 51 and 52).

§ 18. Burning in Systems Consisting of Flat or Cylindrical Layers of Fuel and Oxidizer

Experiments conducted in works [124, 127, 166] showed that it is possible to carry out burning in a system consisting of arbitrarily thick layers of fuel and oxidizer* coming into contact with each other (layer system).

Depending upon properties of components, different methods of preparation of charges were used. If an organic polymer with satisfactory mechanical

*In experimental works [127, 124, 166] and theoretical works [142-145] there was examined the case in which each of the components is not able to burn separately. In experimental work [121] there is studied burning of NH_4ClO_4 in a plexiglas shell. In this case oxidizer is able to independently (in a definite region of pressure). In § 19 we will show that in this case diffusion flame on surface of contact of fuel with oxidizer strongly expands region of stable burning. However, experiments show that in that range of pressures in which burning of NH_4ClO_4 is stable in inert shell, transition to a combustible shell weakly changes burning rate. Therefore, in this case the discussion essentially concerns burning of pure NH_4ClO_4 in the presence of the "torch on duty" on the edges of the charge.

characteristics served as fuel, from it there was prepared a flat or cylindrical shell, where oxidizer was pressed. In other experiments at first there was pressed a tablet of oxidizer and in it a hole was drilled, where under a small pressure a powdery fuel was pressed. If both components were powdery and it was necessary to conduct experiments at small densities, components were poured into a shell with a thin diaphragm (for example, of tracing paper), which divided the components at the time of preparation of charge, but was then removed.

A charge was ignited on the upper end simultaneously all along the extent of the interface with the help of a Nichrome spiral (in experiments with organic fuels) or igniter composition (in experiments with metal powders).

Flame spread down from above along surface of contact of components. In layer of fuel and oxidizer, there were formed wedge shaped cuts inside which there was disposed a zone of burning and which moved together with the flame. Flame propagation velocity along surface of contact of components u attained steady-state value* quickly enough.

For those components (for example, plexiglas) which do not melt before gasification and do not form condensed residue, the form of cut during burning was very clear. Conversely, for such components as $KClO_4$, $KClO_3$, BaO_2 and $KMnO_4$, the form of cut was distorted because of the presence of condensed residue. Thus, burning of systems with $KClO_4$ and $KClO_3$ is accompanied by the formation of big drops of liquid KCl ; from time to time drops are ejected by flow of gas and new ones grow in their place. Burning of systems with BaO_2 and $KMnO_4$ is accompanied by the formation of hard porous slag, the volume of which is close to the volume of initial oxidizer.

Burning rate along surface of contact was measured for the case of plates of transparent fuels with the help of a photoregister [124, 127], and for the case of layers of opaque components with the help of ionization transducers or thin quartz fibers (light conductors), removed from the surface of contact [166].

A. Limiting Conditions of Burning

Limiting conditions for burning along surface of contact of components can be rigid enough. Thus, in a shell of plexiglas it was possible to carry

*Naturally, this speed is not normal burning rate. Moreover for propagation of flame along surface of contact of components, it is impossible to calculate mass burning rate in a natural manner. It is true that it is possible to calculate linear and mass speed of gasification of fuel and (less exactly) oxidizer inside cut (see § 6C and § 9), but this speed characterizes only the process of burning cut, and not process of propagation of flame forward along surface of contact of components. However, even for ordinary disordered systems at $d > d_{min}$, burning rate u is not normal burning rate. Therefore, we will equally designate speed of both processes by lesser u (it is possible to introduce indices when necessary).

out burning (at $p \leq 40$ atm) for not one of a large number of nitrates tested in work [124], although calculated thermal effect for $\text{Pb}(\text{NO}_3)_2$, $\text{Ba}(\text{NO}_3)_2$, $\text{Sr}(\text{NO}_3)_2$ and especially for LiNO_3 is essentially higher than for BaO_2 or KMnO_4 (the latter burn well in a shell of plexiglas even at 1 [atm(abs.)]). This is possibly connected with the fact that during decomposition of nitrates there is given off not oxygen, but comparatively inert nitrogen dioxide. It was not possible to carry out burning in contact with KClO_4 (at $p \leq 60$ atm) with those fuels (polyethyleneterephthalate, galalith, phenolformaldehyde resin and others), during thermal decomposition of which (in presence of oxygen) a large carbonic residue will be formed.

For powders of metals there is a maximum relative density of layer, at which burning becomes impossible (because of excessive heat removal from zone of burning deep into the fuel layer). For powder of tungsten (powder with average dimension of particles ~ 3 microns) in contact with KClO_4 at 20 atm, maximum relative density δ_{max} is approximately 0.5.

Value δ_{max} depends on dimension of layer and on pressure. Let us note that for organic fuels, no maximum relative density is observed, i.e., burning takes place even for a solid plate ($\delta \approx 1$) of fuel. It is normal to connect this with their low (as compared to metals) thermal conductivity.

Conversely, influence of nature of oxidizer on possibility of burning in contact with aluminum or tungsten, apparently, has effect only through change of heat of burning (in any case, there were not observed such shouting contradictions between calculated heat of burning and real ability to burning, as for organic fuels). Data given in Table 53, show that the ability to burn in the systems examined monotonously decreases with increase in expenditures of heat $Q_{\text{p.u.}}$ on decomposition of oxidizer (of the quantity of it which liberates 1 mole of O_2). The higher $Q_{\text{p.u.}}$ the higher the pressure at which burning becomes possible.

B. Dependence of Speed of Flame on Characteristic Dimension of Layer of Components

Experiments were conducted in which thickness d layer of one component was changed at constant thickness of layers of other component (configuration of charges is shown on Fig. 53).

In all cases studied at sufficiently large d there is a plateau on curve $u(d)$ (Fig. 54, 55a, b).*

*Weakening of dependence $u(d)$ at large d was observed also for a rod of aluminum powder in a coaxial shell of BaO_2 [166] (at small d considerable scattering of value u was observed for this system).

Table 53. Ability to Burn of Different Oxidizers in Contact with Aluminum (+++ Very Energetic Burning, Sometimes with Strong Sound; ++ Energetic Burning; + Burning of Moderate Intensity; ± Sluggish Burning, Frequently with Damping; - Burning does not Appear)

Oxidizer and products of its decomposition	Q_{burn} kcal/mole O_2	p. atm.	Result
$KClO_4 \rightarrow KCl + 2O_2$	4.5	0	+++
$Ag_2O \rightarrow 2Ag + 0.5O_2$	14	0	+++
$PbO_2 \rightarrow PbO + 0.5O_2$	24	0	+++
$2KMnO_4 \rightarrow 2MnO + K_2O + 1.5O_2$	33	0	+++
$BaO_2 \rightarrow BaO + 0.5O_2$	38	0	+++
$Ba(NO_3)_2 \rightarrow BaO + N_2 + 2.5O_2$	41.5	0	+++
$MnO_2 \rightarrow MnO + 0.5O_2$	66	0	+
$CuO \rightarrow Cu + 0.5O_2$	75	0	++
$Co_2O_3 \rightarrow 2Co + 1.5O_2$	100 100	0	±
		20	+
$PbO \rightarrow Pb + 0.5O_2$	104	0	+
$Fe_2O_3 \rightarrow 2Fe + 1.5O_2$	130 130	0; 10	-
		20	+
$SnO \rightarrow Sn + 0.5O_2$	136 136	0	-
		20	±
$ZnO \rightarrow Zn + 0.5O_2$	166 166	0; 10	-
		20	±
$Cr_2O_3 \rightarrow 2Cr + 1.5O_2$	182 182	0; 20; 30	-
		50	±

Note. Aluminum (powder) will form internal rod 8 mm in diameter surrounded by a coaxial layer of solid oxidizer with external diameter of 22 mm; both components are taken at bulk density.

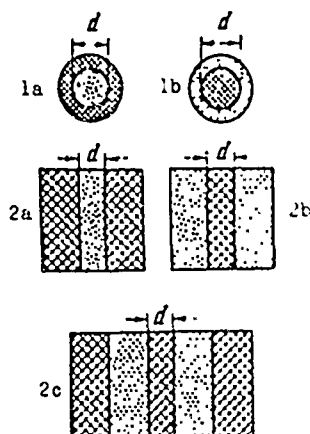


Fig. 53. Configuration of layer systems [124, 127, 166]. 1a - cylindrical rod of oxidizer in coaxial shell of fuel; 1b - cylindrical fuel rod in coaxial shell of oxidizer; 2a - plate of oxidizer between two plates of fuel; 2b - plate of fuel between two plates of oxidizer; 2c - the same as 2b, but two more plates of fuel along the edges.

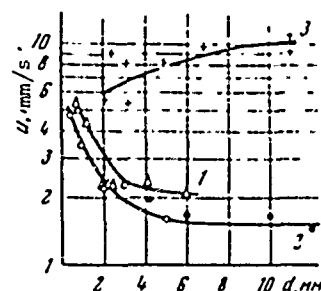


Fig. 54. Dependence u on dimension d of layer of oxidizer [124]. 1 - plate of KClO_4 ($\delta \sim 0.92$)

between two layers of plexiglas (Δ) ($p = 20$ atm); 2 - KClO_4

($\delta = 0.62-0.67$) in flat ($\circ$) and cylindrical ($\bullet$) plexiglas shells ($p = 10$ atm); 3 - BaO_2 ($\delta = 0.35$)

in flat plexiglas cuvette ($p = 20$ atm) (+).

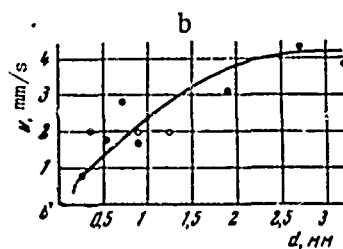
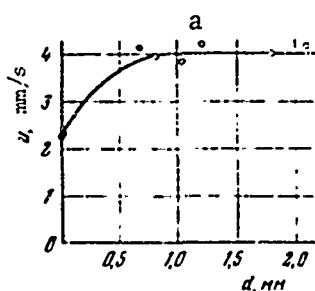


Fig. 55. Dependence u on thickness of plate of fuel (between two layers of KClO_4) ($p = 20$ atm) [124]. a) plexiglas, configuration 2c (see Fig. 53) $\delta_{\text{KClO}_4} = 0.92$; b) polyethylene,

configuration 2b (see Fig. 53) $\delta_{\text{KClO}_4} = 0.84$.

This circumstance is connected with the presence of zone of influence (see § 10B). with increase in width of zone of burning (at the expense of increase in d), burning rate changes only until value $d \text{ ctg } \phi$ (where ϕ is angle of burning out) becomes larger than dimension of zone of influence. In turn dependence $u(d)$ can be used to estimate dimension of zone of influence.

Regarding small d , form of curve $u(d)$ can be different here.

1. For a layer of plexiglas (Fig. 55a) and polyethylene (Fig. 55b) between layers of KClO_4 , and also for a layer of BaO_2 between layers of plexiglas (curve 3 on Fig. 54), burning rate drops with decrease in d .

2. For a layer of KClO_4 between layers of plexiglas (curves 1 and 2 on Fig. 54), burning rate rises with decrease in d .

Causes of different movement of curve $u(d)$ at small d are still vague in many respects for concrete cases; however, it is obvious that for a single layer the form of curve $u(d)$ (at small d) is determined by two competing processes:

a) with decrease in d (for a single layer) total heat emission decreases, whereas thermal losses to external layers remain at approximately the same level. Accordingly, the relative role of thermal losses outside increases;*

b) with decrease in d distance decreases between flames spread along left and right border of layer. Accordingly, thermal losses decrease inside layer d .

C. Dependence of Speed of Flame on Pressure

For layer systems studied in works [127, 124, 166], there were observed all basic forms of curves $u(p)$ known for usual disordered systems.

1. For systems of KClO_4 - plexiglas, polyethylene, polystyrene, vinylplast [no translation found]; KClO_3 - plexiglas; $\text{Ba}(\text{NO}_3)_2$ - Al; KClO_4 - W, burning rate in the range of pressures studied monotonically increased with increase in pressure (see curves 1 and 2 on Fig. 56, and also curve 1 on Fig. 57). The value of index ν (in formula $u = bp^\nu$) for these systems is the following:

Oxidizer,	Fuel	ν	Pressure, atm
KClO_4	Polystyrene	$\sim 1,2$	5 - 40
KClO_4	Plexiglas	1,06	20 - 125
KClO_4	Polyethylene	0,64	10 - 30
$\text{Ba}(\text{NO}_3)_2$	Aluminum	0,49	30 - 100
KClO_4	Polyvinylchloride	0,42	10 - 50

*Conversely, for a system of many layers (the number of which per unit of length of charge increases with decrease in d), total heat emission in zone of influence will increase with decrease in d , and thermal loss outside will decrease.

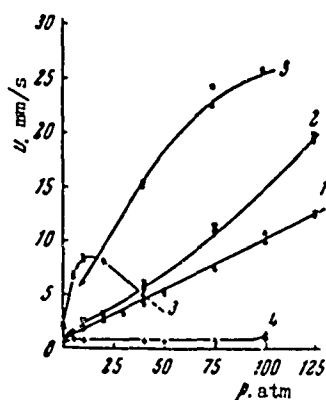


Fig. 56. Dependence $u(p)$ for different oxidizers in cylindrical shell ($d = 6$ mm) on plexiglas [127].
 1 — KClO_4 ($\delta = 0.84-0.88$);
 2 — KClO_3 ($\delta = 0.85-0.89$);
 3 — BaO_2 ($\delta = 0.33-0.34$);
 4 — KMnO_4 ($\delta = 0.53-0.56$);
 5 — stoichiometrical mixture (nongelated) KClO_4 + plexiglas (dimension of predominant share of particles ≤ 10 microns).

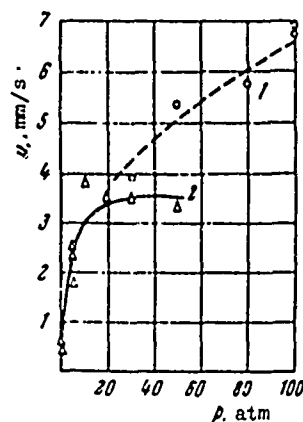


Fig. 57. Dependence $u(p)$ for cylindrical rod ($d = 6$ mm) of fuel in coaxial shell of oxidizer [166].
 1 — system Al (powder, $\delta \approx 0.94$) — $\text{Ba}(\text{NO}_3)_2$;
 2 — system of W (fraction of 140-400 microns; $\delta = 0.40-0.45$) — KMnO_4 ($\delta = 0.94$).

For systems of KClO_4 — plexiglas there was obtained [127, 124]: for flat layers (5-40 atm) $v \approx 0.82$; for cylindrical layers (2.5-20 atm) $v \approx 0.47$; for cylindrical layers (30-125 atm) $v \approx 0.95$.

2. Burning rate for KMnO_4 — plexiglas systems (see curve 4 on Fig. 56), KMnO_4 — W (see curve 2 on Fig. 57) increases only to a certain pressure, and then remains constant in a wide range of pressures.

3. For a BaO_2 — plexiglas system, burning rate at first increases with rise in pressure, but then passes through a maximum and starts to drop (see curve 3 on Fig. 56).

Thus, as in the case of usual disordered mixtures, increase of flame propagation velocity along surface of contact of components is combined with increase of speed of reactions in kinetic zone near "spout" of flame.

Regarding the case in which burning rate of a layer system does not depend on pressure in a certain pressure range up to now it is noted only for systems with KMnO_4 . During decomposition of KMnO_4 a considerable hard residue will

formed. Apparently, flow of oxygen to zone of reaction through layer of solid residue cannot exceed a certain value (i.e., burning takes place in diffusion conditions), which leads to the appearance of a plateau on curve $u(p)$.

Finally, the case of a BaO_2 - plexiglas layer system, in which burning rate passes through a maximum is probably also connected with the presence of solid residue, although it has been impossible up to now to reject another assumption (given in work [127]), according to which reversibility of reaction $BaO_2 \rightleftharpoons BaO + 0.5O_2$ is essential in this case, in consequence of which increase of pressure slows down BaO_2 disintegration and, accordingly, decreases flow of oxygen to zone of reaction.

D. Dependence of Speed of Flame on Density of Layer

During the study of burning in layer systems it is possible to use monolithic plates in not all cases by far.

1. For powders of metals (and, possibly, for powders of certain oxidizers — for example, BaO_2) there is a limiting value of layer density (such that at $\delta = \delta_{lim}$ burning does not take place).

2. There are technological difficulties which, in many cases, limit layer density. For example, during pressing of NH_4ClO_4 or $KClO_4$ into a cylindrical plexiglas shell, value δ_{lim} is not higher than 0.90-0.95. With increase of pressure of pressing higher than 1500-2000 atm, plexiglas starts to flow. For polystyrene, polyethylene, and, all the more so, teflon, the limiting value of δ_{lim} and δ is considerably lower than for plexiglas.

In order to have the possibility to consider influence of porosity of layer on speed of flame along surface of contact special experiments were conducted. It turned out that dependence $u(\delta)$ bears the same character as for volatile or melted VV (see § 2D): in the region of sufficiently large δ mass burning rate $u\delta$ somewhat decreases with decrease in δ (since heat emission drops with decrease in δ , and thermal losses remain approximately constant). However, at certain sufficiently small δ (which are lower the lower the pressure) mass burning rate starts to rise quickly with decrease in δ (since hot products of combustion start to penetrate pores of layer).* Such a form of dependence $u(\delta)$ is obtained for a layer of $KClO_4$ in a cylindrical plexiglas shell (Fig. 58), and also for a cylindrical layer of aluminum in a coaxial shell of $KMnO_4$ (Fig. 59). Let us note that for a layer of $KClO_4$ at 40 atm with decrease in δ , value $u\delta$ after quickly rising passed through a maximum and started to fall (because of fall of total heat emission). It is possible that the same fall

*Accordingly, at a given δ , not very close to $\delta = 1$, dependence $u(p)$ at a certain sufficiently great pressure is sharply strengthened. Such a bend on curve $u(p)$ is obtained for layer systems tungsten (powder, $\delta \approx 0.5$) — $KClO_4$ (at $p > 50$ atm), tungsten (fraction 140-400 microns, $\delta = 0.40-0.45$) — $KMnO_4$ (at $p \approx 100$ atm).

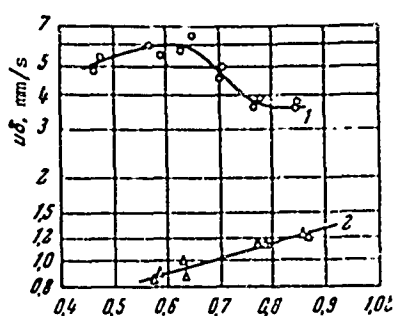


Fig. 58. Dependence $u\delta = f(\delta)$ for KClO_4 in a cylindrical shell ($d = 6$ mm) of plexiglas at different pressures [124]. 1 — 40 atm; 2 — 5 atm.

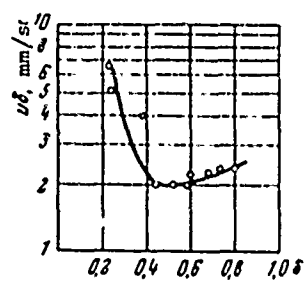


Fig. 59. Dependence $u\delta = f(\delta)$ for a cylindrical rod ($d = 6$ mm) of aluminum powder in a coaxial shell of KMnO_4 ($\delta = 0.94$) at 20 atm [166].

$u\delta$ at very small δ will occur in other cases, too.

E. Comparison of Burning Rate in Layer System and Usual Disordered Mixture

It would be interesting to compare (at $d = \text{const}$) speed of flame along surface of contact of layers of fuel and oxidizer $u_{c,l}$ with burning rate of usual disordered mixture $u_{o,g}$. From theoretical considerations it is obvious [124, 127] that $u_{c,l} > u_{o,g}$, since in disordered mixtures flame is slowed down during transmission of burning through layer of fuel.

However, experimental check of relationship $u_{c,l} > u_{o,g}$ is complex since at small d it is difficult to prepare a layer system, especially one with a large number of layers. With decrease in number of layers — up to a limit of two (layer of oxidizer + layer of fuel) — value $u_{c,l}$ will be understated. It is also necessary to consider that experimental values of $u_{c,l}$ up to now have been obtained only for charges made by pressing powdered oxidizer into a flat or cylindrical channel between plates of fuel. The density of the layer of oxidizer is low (usually $\delta \leq 0.6-0.7$).

Deviation of density from maximum can differently affect $u_{c,l}$ and $u_{o,g}$.

On Fig. 60 there is conducted a tentative comparison of $u_{c,l}$ and $u_{o,g}$ at different d for a KClO_4 — plexiglas system. In this case $u_{c,l} > u_{o,g}$ is satisfied; however, the effect is small. Moreover, for a layer system, data are the most reliable at $d > 4-5$ mm, and for ordinary mixtures, data are most reliable at $d < 0.2-0.5$ mm.

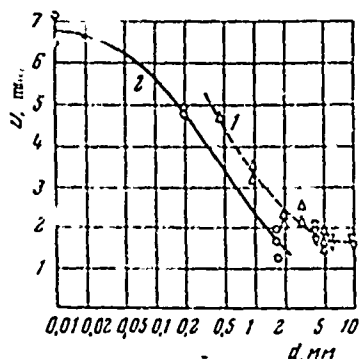


Fig. 60. Comparison of dependence $u(d)$ for layer system and usual disordered mixture [124, 127]. 1 — layer of KClO_4 ($\delta = 0.62-0.67$) thickness d in plexiglas shell ($p = 10$ atm); Δ — flat cuvette; ∇ — cylindrical cuvette; 2 — (gelated) mixture of KClO_4 + plexiglas ($\alpha = 1$; $p = 10$ atm; $\delta \approx 0.90$).

Besides this one should consider that value $u_{c,1}$ is obtained for a single layer of oxidizer (accordingly, $u_{c,1}$ is understated) between two sufficiently thick layers of fuel (surplus of fuel can also lower $u_{c,1}$, since for a KClO_4 — plexiglas system maximum of burning rate lies near $\alpha = 1$).

Furthermore, porosity of layer of oxidizer in layer system ($1 - \delta = 0.33-0.38$) was higher than in usual mixture ($1 - \delta \approx 0.1$) — this could overstate $u_{c,1}$ as compared to $u_{c,2}$ (apparently, not too strongly, since experiments were conducted at low pressure — 10 atm).

Besides the examined type of layer system, in which flame moves along surface of contact of fixed (relatively to one another) layers of components, there was also studied [113] another type of layer system, in which face of oxidizer rod was pressed by spring to face of fuel rod and moved with burning out. For plexiglas and NH_4NO_3 rods there is obtained (at a definite cross section area of rods) a mass speed of gasification of 0.0127 g/s for plexiglas and 0.1755 g/s for NH_4NO_3 (at 70 atm). Such a ratio of mass burning rates corresponds to value $\alpha \approx 1.44$, i.e., burning takes place at essential surplus of oxidizer (NH_4NO_3 is gasified considerably more easily than plexiglas).

§ 19. Burning of Ammonium Perchlorate

Burning of ammonium perchlorate (pure or with small additions of fuels and catalysts) was studied very intensively. It was assumed that burning of pure NH_4ClO_4 is one of the elementary processes going on during burning of mixture systems based on NH_4ClO_4 . Thus, in work [141] it is assumed that burning rate of such systems is simply equal to burning rate of NH_4ClO_4 , taking into account flow of heat from diffusion flame. Such a point of view is useful, but it is absolutely necessary to consider that presence of fuel (burning in diffusion flame) acts on burning rate of NH_4ClO_4 in two mutually opposite directions. At first fuel should be heated and gasified. The fuel takes part of the heat necessary for this away from the $\text{NH}_3 + \text{HClO}_4$ flame (and thereby hampers its burning). However, then fuel reacts in kinetic and diffusion flame; part of

the heat emanated enters the zone of the $\text{NH}_3 + \text{HClO}_4$ flame and increases the temperature in this zone. If the percentage of fuel is close to stoichiometrical percentage the second effect predominates, and the burning rate of NH_4ClO_4 - fuel mixture can considerably exceed the burning rate of pure NH_4ClO_4 . If, however, the percentage of fuel is very small or, conversely, is excessively great (or the fuel is very inert), the first effect predominates, and the burning rate of such NH_4ClO_4 - fuel mixtures can be essentially lower than the burning rate of pure NH_4ClO_4 .

Thus, the regularity of burning of mixtures based on NH_4ClO_4 can be comprehended only if the interaction of mixture components is examined.

Regarding, however, regularities of burning of pure NH_4ClO_4 (without fuel), as will be seen below, they are very distant from regularities of burning of NH_4ClO_4 - fuel.

Burning of pure NH_4ClO_4 bears a clearly expressed limiting character, and, therefore, it is very sensitive to change of conditions of burning. During burning of NH_4ClO_4 samples in an atmosphere of compressed nitrogen, there are a lower and upper limit of pressure such that burning is stable only in the range $p_n < p < p_u$. Values p_n and p_u (and for the upper limit, its very existence) depend on character of shell of charge, diameter of charge, relative density of charge, degree of dispersion of NH_4ClO_4 , etc.

Burning of NH_4ClO_4 is much more sensitive to increase in initial temperature than burning of NH_4ClO_4 mixtures (not too distant for stoichiometry): temperature coefficient β is in the first case, $(5.6-6.0) \cdot 10^{-3} \text{ deg}^{-1}$ [47], and does not exceed $(1-2) \cdot 10^{-3} \text{ deg}^{-1}$ in the second case.

It is equally true that pure NH_4ClO_4 is much more sensitive to the action of additions than compositions based on NH_4ClO_4 (see § 17).

Dependence of burning rate of NH_4ClO_4 on relative density δ , furthermore, testifies to the limiting character of its burning: with decrease in δ there decrease not only mass, but even linear burning rate (whereas for secondary explosives and mixtures, linear burning rate, as a rule, increases with decrease in δ).

Finally, with the introduction into NH_4ClO_4 of small additions of fuel, burning rate can not only not increase, but can even essentially decrease down to damping of burning (since in this case diffusion flame is weakly expressed and does not compensate expenditures of heat on heating and gasification of fuel).

The limiting burning behavior of pure NH_4ClO_4 is connected in the end with the low temperature of its burning (design temperature 1380°K at 1 [atm(abs.)])

9)), the values for compositions based on NH_4ClO_4 , combustion temperature is usually less than 2300-2700°K at 1 [atm(abs.)] [126].

A. Lower and Upper Limits of Burning (Pressure)

There are data concerning lower limit, in works [120, 173, 188, 189, 251] and others. It was found that value p_u decreases:

1) with increase in dimension of NH_4ClO_4 particles [102, 189, 251]. Thus, for example, in work [251] at 20°C, there is obtained:

$d_{\text{NH}_4\text{ClO}_4}, \mu$	<50	50-63	63-100	100-250	250-315
p_u , atm	110	70	70	30	23

The given works [189] are shown in Fig. 61;

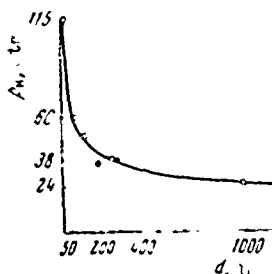


Fig. 61. Dependence p_u on tentative average dimension of particles of NH_4ClO_4 [189]. Experiments in constant pressure bomb; unamored charges $\phi 8$ mm; $\delta = 0.98$.

2) with increase in initial temperature of charge [47, 120, 188, 251]. Thus for example, in work [251] there is obtained (at $d_{\text{NH}_4\text{ClO}_4} < 50$ microns):

$T_0, ^\circ\text{C}$	20	60	100	120
p_u , atm	110	50	30	30

3) with introduction of catalytical additions [47, 173, 190] and others;

4) with increase of diameter (ϕ) of charge. Thus, in work [121] at $\phi = 5$ mm there is obtained $p_u = 50$ atm, and at $\phi = 7$ mm there is obtained $p_u = 30$ atm;

5) with increase in relative density $\delta = \rho/\rho_{\text{max}}$ of charge. Thus, in work [173] at $\delta = 0.65$ there is obtained $p_u = 80$ atm, and at $\delta = 1$ there is obtained $p_u = 60$ atm.

Value p_u can very strongly decrease in the presence of combustible shell (see below).

Furthermore, value p_u depends on character of ignition. Thus, according to work [189], during ignition by incandescent spiral $p_u = 45$ atm, and during use of igniter composition $p_u = 22$ atm.

In respect to upper limit, value p_u (and the presence itself of an upper limit) is influenced by the presence of catalytical additions [120], and also by character of shell [152, 188]. Thus, in work [188] it is revealed that for charge in asbestos shell, upper limit is not observed at least at $p \leq 340$ atm, when for charge without shell $p_u \approx 250$ atm. In work [152] burning of charge without shell faded at $p \geq 280$ atm; on the contrary, in the presence of asbestos shell, it was stable at least up to 1600 atm.

The existence of pressure limits for burning of NH_4ClO_4 undoubtedly, is tied in with losses of heat from zone of burning of $\text{NH}_3 + \text{HClO}_4$. The lower limit apparently, considerably depends on completeness of burning of NH_4ClO_4 , which increases with increase in pressure, of course, up to a definite limit. Thus, for example, in work [188] the composition was investigated of products of combustion of NH_4ClO_4 and it was shown that at 1 [atm(abs.)] (apparently, in the presence of additional radiant flow of heat from projection device) the real composition of products of combustion considerably deviates from the calculated composition ($\text{NH}_4\text{ClO}_4 \rightarrow 0.5 \text{ N}_2 + \text{HCl} + 1.5 \text{ H}_2\text{O} + 1.25 \text{ O}_2$) — the products of combustion contain many oxides of nitrogen. However, with increase in pressure, content of oxides of nitrogen drops, and oxygen content naturally rises (see Table 54).

Table 54. Influence of Pressure on Composition of Products of Burning of NH_4ClO_4

Pressure atm	Number of moles of products per mole of NH_4ClO_4				Temperature
	N_2	N_2O	N_2	O_2	
1	0,55	0,10	0,11	0,65	[188]
35	0,31	0,11	—	0,75	
70	0,23	0,12	—	0,80	
140	0,23	0,05	—	0,80	
1	0,54 (mole NO)	0,145	0,085	0,73	[103]
73,5	0,013 (mole NO)	0,11	—	0,78	

Due to the limiting burning behavior of NH_4ClO_4 , radiation losses can also be essential (radiation of $\text{NH}_3 + \text{HClO}_4$ flame and NH_4ClO_4 surface into the surrounding volume).

The upper limiting is possibly determined by convection losses from the flame zone to the surrounding gas (these losses increase with increase in pressure).

Temperature increase in zone of $\text{NH}_3 + \text{HClO}_4$ flame can considerably expand

limits burning (the upper limit of burning cannot, in general be observed in the whole pressure range studied).

Such a temperature increase in the flame zone can be attained by means of:

- 1) increase in initial temperature of charge;
- 2) additional radiant flow of heat supplied to the charge surface from an external source;
- 3) introduction of catalytical additions, which decrease thickness of zone of burning, thereby decreasing thermal loss from the flame zone. In those cases, in which completeness of burning is low, catalytical additions can increase it;
- 4) additions of fuel* (not too small) or application of a combustible shell;
- 5) decrease in thermal losses from the flame zone through the application of an inert shell with small thermal conduction.

In many works the following particular formulation of the problem is examined: the minimum preheating is clarified at which NH_4ClO_4 becomes combustible at 1 [atm(abs.)]. Thus, in work [47] it is found that pure NH_4ClO_4 ($\delta \approx 0.54$) at 1 [atm(abs.)] burns at $T_0 \geq 200^\circ\text{C}$. If the heat capacity of NH_4ClO_4 is taken at $c \approx 0.26$ cal/g·deg, then preheating is ~ 52 cal/g. In work [103] minimum preheating by increase in T_0 is estimated at 64 cal/g, and by addition of volatile fuel at not less than 107 cal/g (i.e., approximately 1.7 times more). The latter deviation is natural since only part of the heat emanated in the diffusion flame proceeds to the zone of reaction of $\text{NH}_3 + \text{HClO}_4$. Moreover, the flow of heat from diffusion flame is partially used up on preheating and gasification of addition of fuel, and only the remainder of the thermal flow goes into preheating NH_4ClO_4 . The minimum temperature of the NH_4ClO_4 flame at which burning is stable at 1 [atm(abs.)], is $\sim 930^\circ\text{C}$ in the case of volatile fuels; however, in the case of addition of carbon, final temperature of flame should be not lower than 1600°C (since carbon reacts slowly, and part of heat proceeding to surface of charge is small).

In work [188] minimum flow of heat (radiation from projection device)

*We noted above that fuel additions, on the one hand, lead to the appearance of diffusion flame and the appearance of a corresponding thermal flow to the charge surface. However, on the other hand, on heating (and gasification) of fuel, a definite quantity of heat is expended. Therefore, at a small percentage of addition, burning rate can drop with increase in percentage of fuel (up to full damping at those pressures at which burning of pure NH_4ClO_4 is stable). However, at high percentages of fuel the temperature in the $\text{NH}_3 + \text{HClO}_4$ zone, together with its stability and burning rate, start to increase rapidly.

which NH_4ClO_4 could burn at 1 [atm(abs.)] was $10k_{\text{hor.1}}$ cal/cm²·s, where $k_{\text{hor.1}}$ the coefficient of absorption, is approximately equal to $1 - 0.63 = 0.37$ (assuming that the coefficient of transmission is close to zero). Burning rate was ~ 0.2 mm/s. Taking also $\delta \approx 1$ ($\rho \approx 1.95$ g/cm³), we will obtain an estimate for minimum preheating of $10 \cdot 0.37 / 1.95 \cdot 0.02 \approx 95$ cal/g.

Catalytical additions and combustible shell can very greatly expand limits of burning; however, quantitative estimates of temperature increases in zone of flame were not made here.

There is described a rather large number of catalytical additions, which ensure stable burning of NH_4ClO_4 at 1 [atm(abs.)] and room temperature, for example, CuO, Cu_2Cl_2 , MnO_2 , MnCO_3 (see [190], $\delta \approx 0.6-0.65$); Cu_2O (see [173], $\delta \leq 0.84$; [190], $\delta \approx 0.6-0.65$); copper chromite (see [47], $\delta \approx 0.4$), etc.

In work [120] the disappearance of p_* was observed (at least in the range up to $p = 340$ atm) with addition of (3%) copper chromite, CuO, Cr_2O_3 , Fe_2O_3 , MnO_2 and others (with additions $p_* \approx 280$ atm).

A combustible shell very greatly increases burning stability. Thus, in a plexiglas shell (or in the presence of a sufficiently thick film of varnish) NH_4ClO_4 burns stably at least in the range from a few atmospheres [173] up to $p \geq 1000$ atm [121].

B. Burning Rate at Different Pressures

The limiting burning behavior of NH_4ClO_4 leads to the fact that absolute value of its burning rate at different pressures and even the form of curve $u(p)$ itself greatly depend on the conditions under which experiments are carried out (both within the limits of one work and especially during transition from one work to another).*

Let us pause on the form of curve $u(p)$. In spite of very great variety of data, three segments are rather distinctly separated on curve $u(p)$ for NH_4ClO_4 :

1) at "low" pressures, from p_* up to a pressure of 70-200 atm, burning rate monotonously increases with pressure increase. Moreover, in works [120, 121, 173, 188, 189] in the region of "low" pressures, dependence $u(p)$ was close to a direct proportion ($\nu \approx 0.8-1.0$; see Table 55, and also Fig. 62 at $p \leq 150$ atm). However, in work [141] for NH_4ClO_4 charges (5 x 5 mm) without a shell and also in work [121] for NH_4ClO_4 charges smeared with fluorinated lubrication,

*Experiments in works [120, 121, 141, 173, 188, 189] were conducted in a constant pressure bomb and in work [152] in a manometric bomb.

Table 55. Value of Index ν (in Formula $u = bp^\nu$ or $m = b'p^\nu$) for NH_4ClO_4 in Different Shells

$d_{\text{or } \mu}$	Material of shell	Inner diameter of charge, mm	ν			Literature
			"low" pressure	"average" pressure	"high" pressure	
	Plexiglas	7	0.88 (10-15)	when 15-200 atm $\nu < 0$	~ 2.0 (300-950)	[121]
	Layer of perchloro-vinyl varnish	7		~ 0 (100-250)	~ 1.6 (350-1000)	
	Fluorinated lubrication	15				
		7	0.53 (50-200)	0.14 (200-500)	~ 1.3 (500-1000)	[121]
~ 15	Cement + glass	10	0.93 (40-100)			
100-140	The same	10	0.82 (60-100)			
~ 15	Plexiglas	6	0.91 (10-100)			[173]
	$\delta_{\text{NH}_4\text{ClO}_4} \geq 0.95$					
~ 15	Plexiglas	6	0.90-0.92 (5-100)			
	$\delta_{\text{NH}_4\text{ClO}_4} = 0.67 \div 0.74$					[173]
320-410	Plexiglas	6	~ 0.90 (40-100)			
	$\delta_{\text{NH}_4\text{ClO}_4} \geq 0.94$					
	Asbestos	4x4	1.06 (30-50)	0.36 (100-300)		[188]
			0.69 (50-100)			
		16		0.25 (70-350)	1.75 (350-1500)	
53-66	Without shell	5x5	0.585 (70-210)			[152]
66-76		5x5	0.585 (70-210)			
76-104		5x5	0.57 (70-210)			
~ 15		5x5	~ 0.5 (140-210)			[141]
Recrystallized						
~ 15		5x5	0.34 (70-210)			
sample "A"						[141]
~ 15		5x5	0.57 (140-210)			
sample "B"						

Note. The pressure range in atm is shown in parentheses.

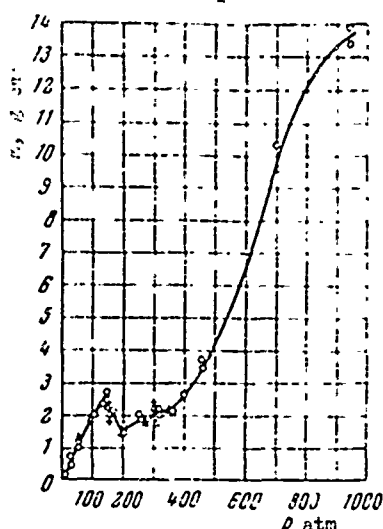


Fig. 62. Dependence $u(p)$ for NH_4ClO_4 (unfractionated) in a shell of plexiglas (internal diameter d ; wall thickness 1 mm; $\delta_{\text{NH}_4\text{ClO}_4} \geq 0.91$) [121]. Δ — $d = 5$ mm; $\circ$ — $d = 7$ mm; $+$ — $d = 10$ mm.

value v (in the 70-210 and 50-200 atm) range, respectively was only 0.34-0.58 (Table 55);

2) at "average" pressures, from 70-200 to 300-500 atm, burning rate continues to increase with pressure rise, but considerably more slowly than at "low" pressures (see Table 55), reaches a plateau (see Fig. 63), drops with pressure

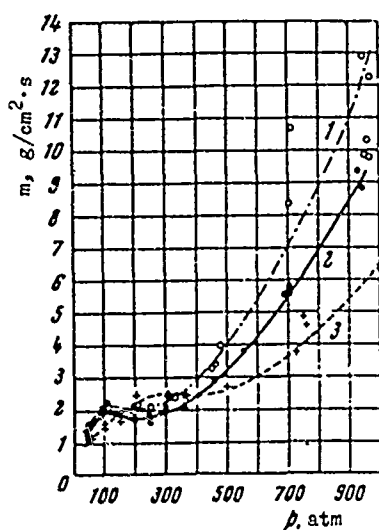


Fig. 63. Dependence $u(p)$ for tablets (diameter d) NH_4ClO_4 (unfractionated, $\delta_{\text{NH}_4\text{ClO}_4} \approx 0.99$), covered by layer of varnish or lubrication [121]. 1($\circ$) — $d = 15$ mm, 0.1 mm thick layer of perchlorvinyl varnish; 2($\bullet$) — the same, but $d = 7$ mm; 3($+$) — $d = 7$ mm, layer of fluorinated lubrication.

rise in a certain pressure range, after which it starts to increase (Fig. 62 at 150-200 atm), or drops with pressure rise up to damping of burning (Fig. 64);

3) at "high" pressures (higher than 300-500 atm), according to works [121, 152], sharp amplification is observed of dependence $u(p)$ (see Table 55 and Figs. 62, 63).

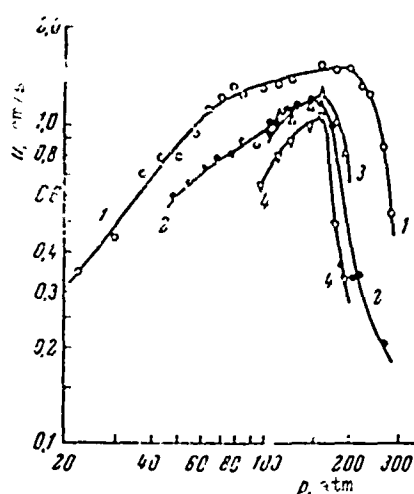


Fig. 64. Dependence $u(p)$ for NH_4ClO_4 ($\delta = 0.97-0.98$; tablet 4×4 mm) without shell [120]. 1 — unfractionated NH_4ClO_4 , 70°C ; 2 — the same, 21°C ; 3 — $d_{\text{OK}} < 53$ microns, 21°C ; 4 — $d_{\text{OK}} = 74-105$ microns, 21°C .

Let us consider the region of "low" pressures in greater detail. In this region, according to many (but not all) works, dependence $u(p)$ is close to dependence $u = bp$, which is characteristic for volatile homogeneous VV. This circumstance is completely natural since NH_4ClO_4 is essentially a weak homogeneous VV.

However, thanks to the limiting burning behavior of NH_4ClO_4 , the analogy with volatile homogeneous VV is limited and easily disturbed.

In particular, according to works [120, 189, 251] burning rate of NH_4ClO_4 can greatly depend on degree of dispersion of the powder from which the charge is pressed (for secondary VV at $\delta \approx 1$, degree of dispersion of initial powder practically does not affect burning rate). Data concerning dependence $u(d_{\text{NH}_4\text{ClO}_4})$, are shown in Fig. 64 and 65. In the case shown in Fig. 65, burning rate at 100 atm changes from ~ 10 mm/s (for fraction 300-3000 microns) to ~ 4.5 mm/s (for fraction 5-250 microns), i.e., approximately 2.2 times.

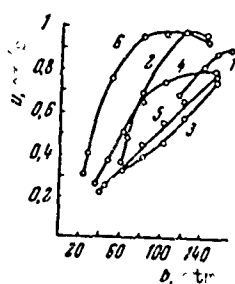


Fig. 65. Dependence of burning rate of NH_4ClO_4 on pressure at different dimension of NH_4ClO_4 particles (charge $\phi 8$ mm without shell; $\delta_{\text{NH}_4\text{ClO}_4} \approx 0.98$) [189]. 1 — 3-7 microns; 2 — 55-95 microns; 3 — 5-250 microns; 4 — 100-300 microns; 5 — 250-400 microns; 6 — 300-3000 microns;

However, from Fig. 64 and 65 it is clear that there is no monotonous dependence between dimension of particles of NH_4ClO_4 and its burning rate, although, apparently, very wide fractions of NH_4ClO_4 have a higher burning rate.

However, essential dependence u on dimension of NH_4ClO_4 particles was not observed in all works. Thus, according to works [141] (105 atm) and [173] (100 atm), degree of dispersion of NH_4ClO_4 had only a weak influence on its

Table 56. Influence of Degree of Dispersion of NH_4ClO_4 Powder from Which Charge is Pressed ($\delta \approx 1$) on Burning Rate

Fraction NH_4ClO_4 , μ	u , mm/s	Material of shell	Diameter of charge mm	Literature
~ 15	12	Cement + glass	10	[173]
< 100	9.9	The same	10	[173]
100-140	10	"	10	[173]
~ 15	11.4	Plexiglas	6	[173]
320-410	12	"	6	[173]
53-66	8.9	Without shell	5x5	[141]
66-76	8.6	The same	5x5	[141]
76-104	7.9	"	5x5	[141]

burning rate (Table 56).

The meaning of influence of dimension of particles on burning rate of NH_4ClO_4 charges pressed up to high density still remains unclear.

According to many authors, the surface of a burning NH_4ClO_4 charge is not flat. It may be that surface area of burning charge depends on dimension of particles of powder from which charge is pressed. This can influence burning rate.

A definite role played by contamination on surface of crystals (which can both delay and increase burning rate). The percentage of contaminations can change in the process of preparing different fractions (for example, it can increase during grinding of NH_4ClO_4 in mills and to decrease during recrystallization).

In many cases it is interesting to compare burning rate of pure NH_4ClO_4 and compositions based on it. From what has been said, it is clear that burning rate of pure NH_4ClO_4 should be determined for the same party and the same fraction which is used in composition.

Nonetheless for tentative appraisals it is possible to use certain average, most frequently encountered, values of burning rate:

P , atm	40	60	80	100
$\bar{u}$, mm/s	4	6	8	10

The meaning of the unusual form of curve $u(p)$ for NH_4ClO_4 at "average" and "high" pressures is still not clear in many respects. For "average" pressures there are convincing considerations on the role of thermal losses due to convection [152, 188]. The more considerable thermal losses due to convection, the more dependence $u(p)$ is weakened, up to full damping. In the presence of a combustible shell [121], burning becomes more stable (as compared to charge without shell), but dependence $u(p)$ is sharply weakened in this case (up to drop in burning rate with rise in pressure in a certain pressure range).

The region of "high" pressures (which is investigated only in works [121] and [152]) is still less clear. Sharp strengthening of dependence $u(p)$, noted in work [152], near 350 atm (exponent ν in formula $u = bp^\nu$ was 0.251 at 70-350 atm, and increased to $\nu \approx 1.75$ at 350-1500 atm), communicated in this work with cracking of NH_4ClO_4 charge resulting from thermal stresses at a high burning rate, and from fast pressure rise in the manometric bomb where the experiments were conducted.

However, sharp strengthening of dependence $u(p)$ at $p > 300$ -500 atm was observed by A. P. Glazkova [121] in a constant pressure bomb. Consequently, accretion of pressure in volume is not a necessary condition for increase in index ν . Furthermore, it turned out that index ν strongly depends on character of shell (for charges in plexiglas shell $\nu_{p=300-500 \text{ atm}} \approx 2.0$; for charges covered by a layer of fluorinated lubrication, $\nu_{p=300-500 \text{ atm}} \approx 1.3$; Table 55). Another essential circumstance is the fact that for NH_4ClO_4 catalyzed 5% $\text{K}_2\text{Cr}_2\text{O}_7$ (according to A. P. Glazkova [227]), curve $u(p)$ at $p \leq 1000$ atm is absolutely "smooth" ($\nu = \text{const} \approx 0.6$) and everywhere goes higher than curve $u(p)$ for pure NH_4ClO_4 . It follows from this that sharp strengthening of dependence $u(p)$ for pure NH_4ClO_4 at $p > 300$ -500 atm should not necessarily be linked with disturbances of laminar burning. It is possible that strengthening of dependence $u(p)$ at "high" pressures (just as weakening of dependence $u(p)$ at "average" pressures) is a result of the limiting burning behavior of NH_4ClO_4 and reflects change of temperature in zone of reaction with rise in pressure. Introduction of a catalyst improves the relationship between heat input and thermal losses, and curve $u(p)$ takes on a "normal" form.

In the preceding division we noted that temperature increase in zone of burning of NH_4ClO_4 by means of increase of initial temperature, catalytical additions, fuel* or application of combustible shell can considerably expand limits of burning.

Temperature increase in zone of burning should naturally also lead to increase in burning rate. This question has been investigated experimentally in the greatest detail at "low" (≤ 70 -150 atm) pressures.

In work [47] dependence on initial temperature is studied for burning rate of NH_4ClO_4 (pure and with addition of 3% copper chromite) at a relative density of $\delta \approx 0.4$; 0.56; 0.95 and a pressure of 1, 20, 40 and 50 atm. In

*See footnote on p. 131.

case. In limits of accuracy of experiment, value of temperature coefficient $\beta = d \ln u / d T_0$ lay approximately in the same range* $\beta = (5,6 \div 6,0) \cdot 10^{-3} \text{ deg}^{-1}$ (Fig. 66). Value β for NH_4ClO_4 is much higher than for mixtures of NH_4ClO_4 with fuels (at α not too far from $\alpha = 1$), where $\beta \approx (1 \div 2) \cdot 10^{-3} \text{ deg}^{-1}$, and than for gas mixtures ($\beta \approx 2 \cdot 10^{-3} \text{ deg}^{-1}$), but is close to value β for liquid nitroesters (see § 2C), where, as we have already noted, burning takes place in two stages, where burning rate is determined by the first, low-temperature stage.

Thus, increase in initial temperature and also introduction of catalytical additions (see § 17) greatly influence both limits of burning and burning rate of NH_4ClO_4 . Otherwise, it is a matter of additions of fuel and application of a combustible shell.

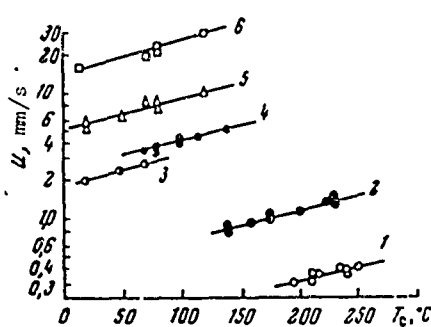


Fig. 66. Dependence of logarithm of burning rate of NH_4ClO_4 (~10 microns) on initial temperature [47]. 1 - $p = 1$ [atm(abs.)] $\delta = 0.56$; 2 - $p = 1$ [atm(abs.)] $\delta = 0.95$; addition of 3% copper chromite; 3 - the same as 2, but $\delta \approx 0.38$; 4 - $p = 20$ atm, $\delta \approx 0.95$; 5 - $p = 40$ atm; $\delta \approx 0.95$; 6 - $p = 50$ atm, $\delta \approx 0.95$, addition of 3% copper chromite.

As we have already noted, small additions of fuel can in certain cases lower burning rate of NH_4ClO_4 (up to damping of burning - in this case limits of burning narrow with pressure). As an example, there can be given experiments with additions of bitumen and urotropine [173] (Table 57 and 58 and Fig. 67).

Causes of such lowering of burning rate were already examined by us at the beginning of this paragraph. It is necessary to direct our attention

*Such constancy of value β is in known degree surprising: it would have been possible to expect that β would decrease with pressure increase and introduction of catalyst, since completeness of burning thereby increase (see above). However, in § 2A, C we showed that temperature coefficient depends on effective temperature in zone of burning. In case of NH_4ClO_4 without fuel, effective temperature can change only within narrow limits, since even at equilibrium composition of combustion products, temperature is very low (1380°K at 1 [atm(abs.)] [150]) and, therefore, already comparatively small lowering of completeness of burning leads to damping of burning (according to the estimate of work [103], burning at 1 [atm(abs.)] is stable only at $T_f \geq 1200^\circ\text{K}$). Accordingly, value β for NH_4ClO_4 without fuel can change only within comparatively narrow limits.

Table 57. Burning Rate of Lean Mixtures of NH_4ClO_4 + Bitumen ($\delta \approx 1$) in Inert Shell (Cement-Phosphate - Glass) [173]

Fraction NH_4ClO_4 , μ	p, atm	u, (mm/s) at bitumen content in % by weight				
		without bitumen	2,2	2,7	3,5	5,3
~ 15	10	0	0	0	3,0	5,5
	40	5,2	0	0	5,2	10,1
	60	7,4	0	0		
	80	10,0	0	0		
	100	12,0	0	7,5	11,7	21,9
100-140	10	0		0		3,6
	40			0		7,1
	60	6,6		5,6		
	80			7,1		
	100	10,0		7,8		13,0
	120			9,6		

Note. Zero means that mixture does not burn at a given pressure.

to the fact that in case of small additions of urotropine (Table 58), the most considerable lowering of burning rate occurs at high pressures (100 atm), and at low pressures (5-10 atm); burning rate can, in general, not be lowered.

Table 58. Burning Rate of Mixtures of NH_4ClO_4 (~15 Microns) + Urotropine (<30-40 Microns) in a Plexiglas Shell [173]
 $\delta \approx 0.95-0.98$, Diameter of Charge is 6 mm

p, atm	u (mm/s) at urotropine content in % by weight					p, atm	u (mm/s) at urotropine content in % by weight				
	0	2	4	10	15,2 (2,2)		0	2	4	10	15,2 (2,2)
5	0,8	0,95	1,0	3,0		5	1,0	3,8	4,2	10,6	
10	1,51	1,42	1,77	6,0		10	11,4	8,4	6,5	28,3	

This result is natural since the higher pressure, the narrower zone of influence (see § 10B) and the less favorable the ratio between expenditures of heat on heating and gasification of particles of fuel and heat addition from zone of

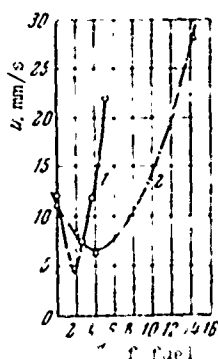


Fig. 67. Dependence of burning rate (at $p = 100$ atm) of lean mixtures of PKhA + fuel on percentage of fuel [173].
1 - bitumen; 2 - urotropine (<30-40 microns).

Let us note that in work [103] data are given about narrowing limits burning and lowering of burning rate with small addition of nonvolatile fuels. A decisive role is assigned to radiation losses, in connection with which influence of color of fuel is emphasized (at a given percentage, black particles can suppress burning, but white particles do not hinder burning).

Regarding combustible shell, it very strongly lowers lower limit of pressure at which burning is still possible (see above), but does not very noticeably affect burning rate at "low" pressures (see, for example, Table 56). In this case heat transfer from diffusion flame to edges of charge is not in a position to increase burning rate of NH_4ClO_4 essentially (and only compensates expenditure of heat on evaporation of fuel), but then does not allow temperature of $\text{NH}_3 + \text{HClO}_4$ flame to go below a certain level ("piot light").

C. Dependence of Burning Rate on Density

In § 2D it is shown that the character of curve $u(\delta)$ (where $\delta = \rho/\rho_{\text{max}}$, relative density of charge) can be different, depending upon conditions of flow of reaction and presence of thermal losses.

If the reaction flows in the gas phase or melt, but thermal losses are absent, $u\delta = \text{const} \neq f(\delta)$. In the same conditions, but in the presence of thermal losses, product $u\delta$ decreases with decrease in δ (since heat emission decreases in proportion to decrease in δ , and thermal losses in the first approximation do not depend on δ and are determined by temperature of flame and environment, character of shell, etc.). However, for secondary VV (see § 2D) linear speed u , as a rule, increases with decrease in δ (on section of laminar burning, not to speak of the section of convection burning where there is observed sharp rise in u and $u\delta$ with decrease in δ).

For NH_4ClO_4 in inert shell, linear burning rate u and, all the more so, product $u\delta$ drops with decrease in δ (Table 59). Stability of burning of NH_4ClO_4

Table 59. Dependence $u(\delta)$ for NH_4ClO_4 (Fraction 100-140 Microns) in Inert Shell [173]
At $\delta \approx 1$ Cement-Phosphate - Glass; at $\delta = 0.75$ and 0.65 - Glass. 10 mm Diameter of Charge

p, atm	u, mm/s			u δ		
	$\delta \approx 1$	$\delta \approx 0.75$	$\delta \approx 0.65$	$\delta \approx 1$	$\delta \approx 0.75$	$\delta \approx 0.65$
60	6,6	4,5	—	6,6	3,4	—
100	10,0	6,7	6,5	10,0	5,0	4,2

*At a high percentage of fuel, burning rate is increased (as compared to burning rate of pure NH_4ClO_4) in the whole pressure range studied, but at low pressures this increase is more considerable than at high pressures (so that, for ratio of burning rate of mixture of NH_4ClO_4 with 14.2 urotropine to burning rate of pure NH_4ClO_4 , we will obtain 5.75 at 5 atm and only 2.5 at 100 atm).

at $\delta = 0.75$ and 0.65 was low; in part of experiments, burning stopped at times charge was not burned completely, scattering of results was great (points given in Table 59 are averages from a large number of experiments).

In plexiglas shell burning of NH_4ClO_4 bears a less limiting character because of the presence of diffusion flame for edges of charge. In this case with decrease in δ burning rate no longer decreases, but increases (Table 60).

Table 60. Dependence $u(\delta)$ for NH_4ClO_4 in Plexiglas Shell (Diameter of Charge 6 mm) [173]

Fraction NH_4ClO_4 , μ	p, atm	u, mm/s		u δ	
		$\delta = 0.95$	$\delta = 0.72$	$\delta = 0.95$	$\delta = 0.72$
15	5	0.68	1.0	0.65	0.72
	10	1.5	1.6	1.41	1.15
	40	4.9	5.9	4.7	4.25
	100	11.4	12.6	11.0	9.1
320-410	5	0.63	0.78	0.6	0.56
	10	1.04	1.55	1.0	1.1
	40	5.4	Passage of burning	5.2	—
	100	12.0	The same	11.5	—

Product $u\delta$, although it decreases with decrease in δ , is considerably weaker than for NH_4ClO_4 in inert shell. Regarding stability of burning, NH_4ClO_4 in plexiglas shell at $\delta > 0.7$ completely burns already at several atmospheres pressure, whereas burning of NH_4ClO_4 in inert shell (or without any shell) does not go lower than 20-40 atm. Scattering of results for NH_4ClO_4 in plexiglas shell is essentially lower than in inert shell.

If with NH_4ClO_4 there is mixed a sufficiently effective catalytical addition, zone of burning narrows. Accordingly, thermal losses decrease. In a number of cases, completeness of burning is increased. Therefore, burning of catalyzed NH_4ClO_4 can be completely stable in inert shell at low pressures, but product $u\delta$ remains constant with decrease in δ .

Thus, for NH_4ClO_4 (~15 microns) with addition of 2% Cu_2O in work [173] there is obtained (p = 1 [atm(abs.)]; glass shell ϕ 10 mm):

δ	0.84	0.62	0.59	0.54	0.38
$u\delta$, mm/s	0.92	0.98	0.94	0.94	0.95

Finally, experiments were conducted with pure NH_4ClO_4 in inert shell, but at raised initial temperature. There was obtained the natural result

that product $u\delta$ drops less with decrease in δ the higher T_0 (compare Tables 59 and 61).

At 150°C mass: burning rate almost does not depend on δ .

Table 61. Dependence $u(\delta)$ for Pure NH_4ClO_4
in Inert Shell at Raised Initial Temperature
(Pressure 20 atm) [173]

δ	$u\delta$, mm/s	T_0 , °C	δ	$u\delta$, mm/s	T_0 , °C
0,98	3,3	100	0,98	4,4	150
0,75	2,9	100	0,62	4,2	150
0,62	2,5	100			

Results of experiments concerning dependences $u(\delta)$ will agree with ideas about the fact that burning of NH_4ClO_4 takes place in the gas phase and is very sensitive to thermal losses. If the leading reaction took place in the condensed phase, then increasing initial temperature or adding catalyst could increase absolute value of burning rate, but could not give $u\delta = \text{const}$.

* * *

In conclusion of this paragraph, one should note that in spite of low combustion temperature and sensitivity to thermal losses, absolute value of burning rate of NH_4ClO_4 is sufficiently great. At 40-100 atm it lies within the same limits as burning rate of volatile VV (such as PET', tetryl — see Table 13) and noticeably exceeds burning rate of such VV as dyne, picric acid, trotyl — see the same), although the combustion temperature for these VV is 1.5-2.5 times higher than for NH_4ClO_4 . However, as we have already noted, burning of many VV containing the NO_2 group takes place in two stages, where burning rate is determined mainly by the first, low-temperature stage. In § 2A, we noted that burning rate of volatile VV, in turn, is apparently close to burning rate (mass) gas of mixtures based on NO_2 . Conversely, as compared to burning rate (mass) of gaseous mixtures with oxygen (see Table 4) and, apparently, with HClO_4 (see beginning of § 10), burning rate of NH_4ClO_4 is small (or very small), although a reliable comparison cannot be made due to scantiness of experimental data. The burning rate of NH_4ClO_4 (even without catalyst) is considerably higher than (4-5 times) than the burning rate of NH_4NO_3 (with catalytical additions).

Finally, if one were to compare the burning rate of NH_4ClO_4 with the burning rate of mixtures of NH_4ClO_4 with fuels, then (as we noted at the beginning of this paragraph), depending upon the percentage of fuel and its properties,

are are possible the most diverse ratios between these burning rates. Very small additions of fuels can considerably lower the burning rate of NH_4ClO_4 .

Mixtures close to stoichiometry can have a burning rate significantly higher (2-4 times) than that of NH_4ClO_4 (certainly, the burning rate of mixtures strongly depends on degree of dispersion of components and also on activity of fuel and heat of its combustion, on expenditures of heat of heating of fuel and, in case of volatile fuels, on its gasification, etc.). Conversely, the burning rate of mixtures with a large surplus of fuel can be considerably lower than the burning rate of pure NH_4ClO_4 .

§ 20. Burning Rate of Smoky (Black) Powder

Black powder is a mixture of KNO_3 , charcoal and sulfur. The ratio of components in it can change somewhat. The usual composition is 75% KNO_3 , 15% charcoal, 10% sulfur (this composition is close to [DRP-1] (ДРП-1) and DRP-3 powder).

Smoky powder is the oldest mixture system, which during many centuries was used both as powder and as explosive. Today the application of black powder is very limited. It is used (see [219]) in time fuses, in igniters, in (Bickford) fuses, in hunting weapons, etc.

The study of burning of smoky powder, besides direct interest, is useful for understanding regularities peculiar to those systems, in the zone of burning of which there are carbon particles.

It is also important that a series of theoretical works [65, 225, 226] was carried out specially for black powder. Therefore, consideration of experimental data for black powder makes it possible to compare theory with experiment.

A. Dependence on Pressure

In early works (results of which are given in [219]) it was already noted that for smoky powder dependence $u(p)$ at low pressures is strong, but is weakened with rise in pressure. Thus, according to St. Robert, at pressures lower than atmospheric, the value of index ν (in formula $u = bp^\nu$) is close to $\nu = 0.7$. At high pressures, according to V'yel' $\nu = 0.3-0.5$.

Baum and Levkovich [220] give for smoky powder at 1 [atm(abs.)] value $\nu = 0.505$ and at high pressures (in manometric bomb) $\nu = 0.117$.

Shapiro [220] on the basis of treatment of data of a number of authors arrived at the following results:

$p, \text{ atm}$	0,4	1,0	2,0	3,0	500
ν	1,00	0,63	0,49	0,40	0,33

According to Andreyev [221], for a safety fuse at $p < 2-2.5$ atm $\nu = 0.5$, and above this pressure, $\nu = 0.24$.

Weakening of dependence $u(p)$ for black powder with increase in pressure is also noted in later works [42, 44, 163]. Thus, for coefficients b and ν in formula $u(\text{mm/s}) = bp^\nu$ (atm) the following values are obtained:

	[163]	[42]	[44]	[44]
p , atm	0.25-5	10-1000	4000-20000	1500-4500
ν	0.5	0.216	0.25	~0.0
b	8.8	2.3 *	8.0	~60

Experiments in works [42, 163] were conducted in a bomb of constant pressure; in work [44] experiments were performed in a variable pressure bomb.

In work [42] DRP-1 powder is investigated in work [44] DRP-3 powder is investigated.

Experimental points obtained in works [42, 44, 163], are plotted in Fig. 68 at coordinates $\lg u$, $\lg p$. One may see well enough the weakening of dependence

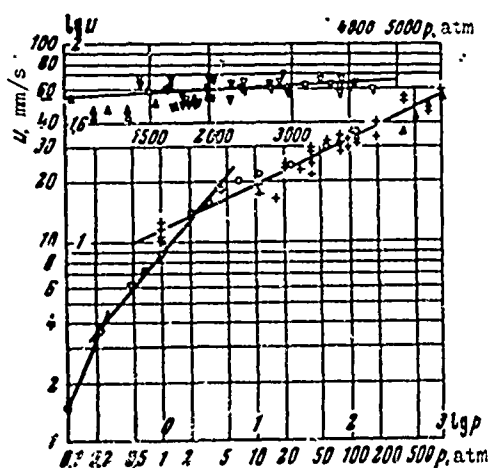


Fig. 68. Dependence of burning rate of black powder on pressure. $\circ$ - present work [163]; $+$ - present work [42]; Δ , ∇ - present work [44] (for two different variable pressure bombs); data in interval the 1000-4000 atm range are given above on a larger scale (along the p axis).

$u(p)$ with rise in pressure. Curve $\lg u = f(\lg p)$ can be approximated by broken line consisting of four segments. Value ν is:

p , atm	0.1-0.25	0.25-3	1-1000	1000-4000
ν	1.08	0.55	0.226	0.118

In spite of considerable scattering of experimental points, the most reliable data, undoubtedly, are those in the 1-1000 atm range, since here straight line $\nu = \text{const}$ is drawn on the basis of results of three independent works.

For a model KNO_3 - charcoal mixture (black powder without sulfur), there are data on dependence of exponent ν (in formula $u = bp^\nu$) on ratio of components [163]:

*Value b' is given for formula $m (\text{g/cm}^2 \cdot \text{s}) = b' p^\nu (\text{atm})$.

% KNO ₃ / % carbon . . .	92/8	85/15	76/24	68/32
α^1	2,13	1,05	0,59	0,39
γ	0,57	0,5)	0,23	0,39
Pressure, atm	12,5-10)	5-125	1-10)	1-100)

Thus, with increase in fuel surplus, dependence $u(p)$ for KNO₃ - charcoal mixtures is weakened (analogously the way this took place in the presence of a high enough fuel surplus for KClO₄ - graphite and KClO₄ - tungsten mixtures; see § 14).

B. Dependence on Initial Temperature

At moderate initial temperatures (and pressure not exceeding atmospheric pressure too much) dependence $u(T_0)$ is very weak for black powder:

	[159]	[159] **	[224]	[224]
P, atm	1	—	1	10
T, °C	0-10)	-31-3 : 44	20-115	21-125
$\beta \cdot 10^3$, deg ⁻¹	1,5 ± 0,4	0,65	0,5)	~1,0

However, judging by the present work [224], at higher T_0 dependence $u(T_0)$ can be essentially strengthened (for example, at 1 [atm(abs.)] $\beta_{20-115^\circ\text{C}} = 0.50 \cdot 10^{-3}$ deg⁻¹, and $\beta_{115-250^\circ\text{C}} \approx 1.9 \cdot 10^{-3}$ deg⁻¹; at 10 atm $\beta_{75-225^\circ\text{C}} \approx 3 \cdot 10^{-3}$ deg⁻¹).

In work [224] there is also studied dependence $u(T_0)$ for "sulfur-free" powder containing 85% KNO₃ and 15% charcoal. At 1 [atm(abs.)] and moderate initial temperatures, value β for "sulfur-free" powder is essentially higher ($\beta_{20-115^\circ\text{C}} \approx 4 \cdot 10^{-3}$ deg⁻¹) than for ordinary powder ($\sim 0.5 \cdot 10^{-3}$ deg⁻¹). At high T_0 , values β for "sulfur-free" powder (KNO₃ - charcoal) reach $7 \cdot 10^{-3}$ 1/deg. It is necessary, however to emphasize that data on dependence $u(T_0)$ for high T_0 has up to now been obtained in only one work [224], and, therefore, there is no possibility of estimating their reliability.

C. Dependence on Composition

In work [163] experiments were conducted with black powder of ordinary composition (75% KNO₃, 15% charcoal, 10% sulfur; for this composition, value α is ~ 0.7) and binary KNO₃ - charcoal mixtures at ratio 92:8, 85:15, 76:24, 68:32 (value α is 2.1; 1.05; 0.6; 0.4).

*For calculation of α the following element composition of charcoal is accepted: C₆H₂O.

**According to F. A. Baum.

From the point of view of heat of burning, sulfur is much less profitable than carbon (heat of burning of a S - KNO_3 stoichiometrical mixture of a 100 cal/g, and for a C - KNO_3 stoichiometrical mixture ~370 cal/g). Nonetheless, it turned out that the burning rate of ordinary black powder (with 10% sulfur) in the pressure range investigated (1-125 atm) is essentially higher (see direct 1 on Fig. 69) than the burning rate of KNO_3 - charcoal binary mixtures at a

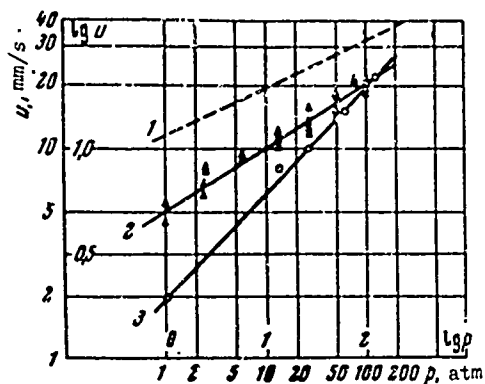


Fig. 69. Comparison of burning rate of ordinary black powder (with gray powder) and KNO_3 + charcoal binary mixtures [163]. 1 - ordinary black powder (data are transferred from Fig. 68); 2 - mixture of 76% KNO_3 + 24% charcoal; 3 - mixture of 85% KNO_3 + 15% charcoal.

ratio of components of 85:15 ($\alpha \approx 1.05$ - see straight line 3 on Fig. 69) and 76:24 ($\alpha \approx 0.6$ - see straight line 2 on Fig. 69). For mixture 76:24 (which for value α is sufficiently close to powder with sulfur and can be compared with it) value $\nu \approx 0.28$ lies close enough to value ν for black powder ($\nu \approx 0.23$ in the 1-1000 atm range). Therefore, it is possible to expect that difference in burning rates of ordinary powder (with gray powder) and "sulfur-free" powder will be preserved at higher pressures.*

The reasons why sulfur considerably accelerates burning of KNO_3 - charcoal mixture has not yet been satisfactorily explained, in spite of the centuries-old history of the use of black powder.

It is necessary to emphasize that finely divided charcoal is, in itself, a very active fuel:

1) a KNO_3 - charcoal stoichiometrical mixture already burns fast at 1 [atm(abs.)]. Conversely, stoichiometrical mixtures of KNO_3 with bitumen, paraffin, and graphite are incapable of stable burning at $p \leq 100$ atm (and room temperature), and also at $T_0 \leq 200^\circ\text{C}$ (and 1 [atm(abs.)]);

*Conversely, for "sulfur-free" powder with ratio of components 85:15 value ν is considerably higher ($\nu \approx 0.50$) than for ordinary powder ($\nu \approx 0.23$). Therefore, the difference in burning rates of these two compositions is quite considerable at 1 [atm(abs.)] (~2 mm/s for "sulfur-free" powder, 85:15 and ~10 mm/s for ordinary powder), quickly decreases with rise in pressure. It is possible that at a pressure of several hundreds of atmospheres, line 3 on Fig. 69 ("sulfur-free" powder 85:15) will intersect line 1 (ordinary powder) and will go above it, in accordance with heat of burning. However, of course, value α for composition 85:15 is much closer to stoichiometry than for ordinary powder, and their comparison is not correct.

2) it is well-known that mixtures of ammonium nitrate with different organic fuels can burn stably only in the presence of a catalyst (for example, $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$) and at not too low a pressure. However, a mixture of NH_4NO_3 with charcoal at $\alpha = 1$ burns stably even at 1 [atm(abs.)] (according to A. P. Glazkova). It is natural, however, that burning rate for this composition is much lower than for analogous KNO_3 or KClO_4 compositions (at 25 atm the burning rates of the compositions shown are approximately equal to 1, 10 and 14 mm/s);

3) a stoichiometrical mixture of KClO_4 with charcoal (see curve 1 in Fig. 70) in the 1-24 atm range burns faster* than a mixture of KClO_4 with bitumen (curve 2 on Fig. 70).

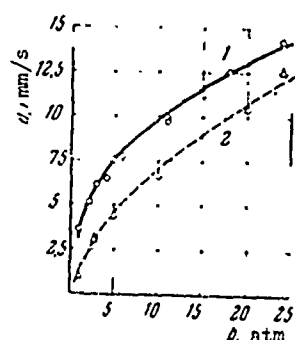


Fig. 70. Comparison of burning rate of finely divided stoichiometrical mixtures of KClO_4 with charcoal (1) and bitumen (2) [163].

It is necessary to take note, however, that in the pressure range examined, value v for KClO_4 - charcoal mixture ($v = 0.44$) is essentially lower than for KClO_4 - bitumen mixture ($v = 0.64$). Therefore, at higher pressures, possibly, KClO_4 - bitumen mixture will burn faster than KClO_4 - charcoal mixture.

4) small additions of charcoal can considerably increase the burning rate of a number of condensed systems, including those containing a large fuel surplus (for example, for NH_4ClO_4 + plexiglas mixture $\alpha = 0.6$ [175]).

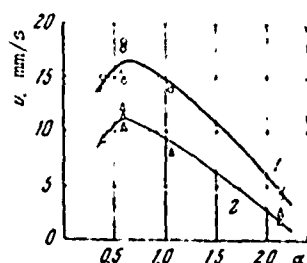


Fig. 71. Dependence of burning rate of a finely divided KNO_3 + charcoal mixture on the ratio of components at different pressures [163]. 1 - 50 atm; 2 - 12.5 atm.

*Let us note that burning rate of KClO_4 - charcoal stoichiometrical mixture at 1-25 atm is essentially higher than the burning rate of an analogous KNO_3 mixture, but, at the same time, lower than the burning rate of ordinary black powder (with gray).

For KNO_3 - charcoal mixtures, it is possible to construct approximately curves $u(\alpha)$ (Fig. 71). Maximum burning rate lies near $\alpha = 0.6$, i.e., essentially nearer to stoichiometry than $u_{\max}$ for a KClO_4 - graphite mixture (there $u_{\max}$ lies near $\alpha = 0.4$ [175]).

D. Comparison with Theory

A theoretical expression for the burning rate of black powder (as a function of pressure and dimension of carbon particles) was obtained for the first time by O. I. Leypunskiy [65]. The natural assumption was accepted that at first there occurs gasification of oxidizer and then carbon particles burn in the flow of products of gasification of oxidizer above surface of charge.

Proceeding from the basic assumption that burning rate is proportional to square root of speed of liberation of heat in zone of reaction (in analogy with the theory of Zel'dovich - Frank-Kamenetskiy, see § 1E), an expression was obtained for burning rate of finely divided* powder. For diffusion conditions of burning of carbon particles, burning rate of powder $u \sim \sqrt{p/d}$, for kinetic conditions (reaction of first order) $u \sim p/\sqrt{d}$.

We noted that experimental value v is close to one at pressures lower than atmospheric pressure and close to $v = 0.5$ at pressures of several atmospheres (at higher pressures experimental value v decreases). It is possible to assume that value $v \approx 1$ in vacuum corresponds to kinetic conditions and value $v \approx 0.5$ at 1-5 atm corresponds to diffusion conditions. Decrease in v at higher pressures in work [65] is not explained. However, it can be understood, taking zone of influence into consideration (see § 10B). Actually, with increase in pressure the dimension of the zone of influence decreases more and more and velocity of particles of fuel (at constant dimension) will lag behind speed of gas more and more. At very high pressures, particles are practically stationary within limits of zone of influence. In this case, as can be seen from § 8B, burning rate does not depend on pressure, i.e., $v = 0$.

Regarding dependence $u(d)$, the influence of dimension of carbon particles on burning rate was almost not investigated experimentally. However, test experiments [137] indicate that experimental dependence $u(d)$, apparently, is considerably weaker** than $u \sim d^{-1}$.

*Dimension of particles d of carbon is so small that their speed can be considered equal to speed of gas.

**Two mixtures of identical composition (85% KNO_3 + 15% charcoal) were investigated. One mixture had dimension of particles of fuel and oxidizer ~ 10 -20 microns, and the other had dimension ~ 400 microns. At 1-50 atm burning rate for finely divided mixture was only approximately 2 times higher than for coarsely divided mixture (at 50 atm $u_M \approx 16$ mm/s, $u_{KP} \approx 8$ mm/s), although particle dimension differed by tens of times.

In a wor. of B. V. Novozhilov [225], which was a continuation of work [65], an attempt was made to obtain a solution without assuming that carbon particles move with speed of gas. For kinetic conditions there was obtained

$$u \sim p_0 \sqrt[3]{d}, \text{ for diffusion conditions there was obtained } u \sim \sqrt[3]{p_0 d}.$$

However, in his later work, B. V. Novozhilov [226] discovered these results to be incorrect (inasmuch as calculation of acceleration of particles by gas flow was conducted inaccurately) and for diffusion conditions returned to the expression, $u \sim \sqrt{p_0 d}$, obtained in work [65].

In work [226] an attempt is also made to calculate absolute velocity of burning of black powder, proceeding from the assumption that ignition temperature of carbon particles can be calculated with the help of the criterion of Frank-Kamentskiy. The computed value of burning rate turned out to be considerably lower than the experimental value. Hence, it was concluded that carbon particles ignite earlier than this criterion would indicate.

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

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

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

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