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# TRANSLATION

COMBUSTION IN LIQUID-PROPELLANT ROCKET MOTORS

By

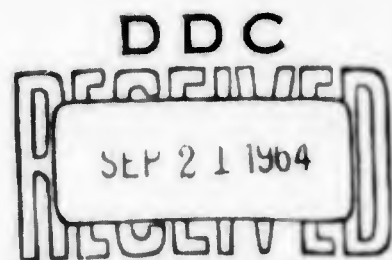
Yu. Kh. Shaulov and M. O. Lerner

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# EDITED MACHINE TRANSLATION

COMBUSTION IN LIQUID-PROPELLANT ROCKET MOTORS

BY: Yu. Kh. Shaulov and M. O. Lerner

English Pages: 235

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PREPARED BY:

TRANSLATION DIVISION  
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WP-AFB, OHIO.



Yu. Kh. Shaulov i M. O. Lerner

GORENIYE V ZHIDKOSTNYKH RAKETNYKH DVIGATELYAKH

Gosudarstvennoye  
Nauchno-Tekhnicheskoye Izdatel'stvo  
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## TABLE OF CONTENTS

Conventional Symbols.....	1
Preface.....	4
Chapter I. Elements of Kinetics of Chemical Reactions.....	7
1. Activation Energy.....	7
2. Monomolecular Reactions.....	12
3. Bimolecular Reactions.....	15
4. Recombination of Atoms and Radicals.....	17
5. Chain Reactions.....	19
1. Non-Branching Chain Reactions.....	20
2. Branched Chain Reactions.....	22
3. Chain Reactions With Degenerate Branchings.....	25
6. Chain Self-Ignition.....	26
7. Thermal Self-Ignition.....	28
Chapter II. Homogeneous and Heterogenous Combustion.....	32
1. Theory of Normal Speed of Flame of Zel'dovich and Frank-Kamenskii.....	34
2. Dependence of Normal Speed of Flame Upon Parameters of Combustible Mixture.....	40
1. Dependence of Normal Speed of Flame on Pressure.....	40
2. Dependence of Normal Speed of Propagation of Flame on Temperature.....	42
3. Dependence of Normal Speed of Flame on Composition of Mixture.....	43
4. Action of Various Impurities on Speed of Flame.....	45
3. Theory of Limits of Propagation of Flame.....	47
4. Stability of Normal Front of Flame.....	54
5. Turbulent and Detonation Combustion.....	64
1. Turbulent Combustion.....	64

2.	Ignition of Two-Phase Mixtures.....	69
3.	Burning of Atomized Fuel.....	79
4.	Elements of Theory of Detonation.....	82
Chapter III. Kinetics of Chemical Reactions in Flame.....		88
1.	Structure of Front of Flame.....	88
2.	Method of Studying Kinetics of Chemical Reaction in a Flame.....	95
3.	Burning of Mixtures With Oxides of Nitrogen.....	99
1.	Kinetics of Decomposition and Formation of Nitric Oxide.....	100
2.	Decomposition of Nitric Oxide in Flame.....	102
3.	Mechanism of Reaction in Flame of $\text{NO} + \text{H}_2$ .....	104
4.	Decomposition of Nitrogen Peroxide in Flame.....	105
4.	Two-Flame Burning.....	106
1.	Critical Conditions of Ignition of Mixtures of Nitric Oxide....	113
2.	Effect of Self-Retardation of Reaction in Flame.....	114
Chapter IV. Carburetion.....		121
1.	Atomization of Fuel.....	122
1.	Movement of Liquid in Fuel Supply System.....	123
2.	Mechanism of Formation of Drops.....	124
3.	Characteristics of Atomization.....	129
4.	Modeling of Process of Atomization.....	132
2.	Evaporation of Fuel.....	134
1.	Isothermal Evaporation of Drops.....	135
2.	Evaporation of Totality of Drops.....	141
3.	Mixing.....	143
4.	Delay of Ignition.....	148
1.	Methods of Determination of Delay of Ignition.....	150
2.	Factors Having an Effect on Delay of Ignition.....	152

Chapter V. Steady-State Regime of Burning.....	155
1. General Concepts.....	156
2. Experimental Investigations.....	168
Chapter VI. Instability of Combustion Process.....	173
1. Analysis of Low-Frequency Instability.....	180
1. Equation of the Combustion Chamber.....	181
2. Equation of Motion of Components Along Pipe Lines.....	183
3. Determination of Boundary of Stability.....	186
2. "Intrachamber" Instability.....	190
3. Analysis of High-Frequency Instability.....	193
1. Differential Equations of Combustion Chamber.....	194
4. Analysis of Instability of a System With Distributed Parameters in Pipe Lines.....	197
5. Criterion of Shchelkin.....	201
6. Experimental Research of Stability of Process of Burning.....	203
1. Measurement of Time of Delay.....	204
2. Experimental Observations.....	208
Chapter VII. Simulation of Process of Burning.....	211
1. Main Aspects of Theory of Physiochemical Similarity.....	214
2. Conditions of Similarity of Two-Component Liquid Rocket Engine.....	222
Literature.....	225

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## CONVENTIONAL SYMBOLS

E -- activation energy;	t -- time;
R -- universal gas constant;	$\tau$ -- period of induction; time lag;
v -- volume;	$\mu$ -- coefficient of discharge;
p -- pressure;	$r_c$ -- radius of nozzle;
k -- constant of chemical reaction rate;	$r_{bx}$ -- radius of inlet nozzle;
$\tau^*$ -- lifetime of excited molecule;	G -- discharge;
u -- chemical reaction rate; speed of propagation of flame;	$\Delta p$ -- pressure drop;
$u_b$ -- speed of flame relative to combustion products;	$\nu$ -- coefficient of kinematic viscosity;
$u_n$ -- normal speed of flame;	$\eta$ -- coefficient of dynamic viscosity;
Z -- total number of collisions;	$\gamma$ -- index of adiabatic line;
$W_0$ -- rate of formation of active centers;	M -- Mach number;
f -- rate constant of branching of chain;	Re -- Reynolds number;
g -- rate constant of termination of chain;	Pe -- Peclet criterion;
$\phi$ -- rate of heat emission;	We -- Weber criterion;
Q -- reaction energy ;	Nu -- Nusselt number;
$\lambda$ -- thermal conduction	Pr -- Prandtl number;
c -- heat capacity; concentration;	D -- Damköhler criterion
$\rho$ -- density;	Fr -- Froude criterion;
$\kappa$ -- coefficient of thermal diffusivity;	Ka -- Karman number;
$\delta$ -- zone of preliminary heating;	x -- spatial coordinate;
$T_0$ -- ignition temperature;	v -- velocity of flow;
	$p$ -- pressure
	$\beta$ -- coefficient of evaporation;

$T_r$  -- combustion temperature  
 $f/v$  -- ratio of surface of flame to volume;  
 $b$  -- scale of splitting;  
 $C^*$  -- characteristic velocity;

$\lambda$  -- coefficient of thermal conductivity;  
 $a$  -- coefficient of heat transfer;  
 $n$  -- index of interaction.

## Indices

- |                                                                  |                                                                             |
|------------------------------------------------------------------|-----------------------------------------------------------------------------|
| r -- gas; fuel;                                                  | k -- chamber                                                                |
| $\Phi$ -- afterburner;                                           | c -- nozzle;                                                                |
| o -- oxidizer;                                                   | 6 -- tank                                                                   |
| Kp -- critical section;                                          | n -- outflow;                                                               |
| -- line above letter signifies<br>average or steady-state value; | p -- symbolic representations of<br>differentiation in operational<br>form; |
| s -- complex quantity, which is a<br>Laplace transform variable. |                                                                             |



## PREFACE

On 4 October 1957, by the launching of Soviet artificial Earth satellite first in history of humanity was realized the prophetic foresight of founder of present day rocketry -- Constantine Eduardovich Tsiolkovskiy. After first satellite were launched second and third, and also there was created artificial planet. Space rocket placed a pennant with Emblem of Soviet Union on Moon, automatic interplanetary station (APS) photographed its reverse side. There was launched an APS to planet Venus. On 12 April 1961, for the first time in history was placed in orbit an Earth satellite, the Soviet space ship "Vostok" with pilot-astronaut Yu. A. Gagarin. Ship together with pilot-astronaut on this day safely landed in a given region of Soviet Union. These immortal feats of the Soviet people opened for humanity the road into cosmic space.

The creator of the main propositions of rocket dynamics and theory of liquid-propellant rocket motors, K. E. Tsiolkovskiy, deeply believed that his labors in rocketry and interplanetary communications would be completed by Soviet scientists.

Our scientists played important role not only in development of main propositions of K. E. Tsiolkovskiy, but also in development of theory of combustion, whose value for operation of liquid-propellant rocket motors is incomparably. Efficiency and stability of operation of motor to a great extent depend on organization of the working process of combustion.

By efforts of Soviet scientists were developed ideas of application of chemical kinetics to problems of combustion and explosions in motors there was constructed rational theory of propagation of flame, there was planned the synthesis of chemical kinetics, on the one hand, and hydrodynamics, heat transfer and diffusion, on the other hand.

In spite of serious advances in development of our ideas concerning combustion of atomized fuel, solution of problems connected with creation of efficient motors requires intense labor and a great expenditure of time. Theory of combustion in its contemporary state gives only qualitative directions for these works.

In this book are expounded elementary bases of theory of combustion of homogeneous gas mixtures and working processes proceeding in liquid-propellant rocket engines. In it are considered thoroughly indisputable ideas of chemical kinetics and are expounded main characteristics of propagation of flame, the knowledge of which is necessary in the study of and interpretation of complicated physicochemical phenomena observed during combustion of two-phase mixtures in the chamber of a rocket motor.

In the motor, the picture of combustion abruptly is distorted by phenomena of a hydrodynamic character, and here very frequently the kinetics of chemical processes moves to the background. The rate of a process and its subsequent intensification are limited by processes of heat transfer and mass transfer. Study of characteristics regulating such a combined time-dependent characteristics. An example of the application of such quantities is the hydrodynamic theory of stability.

Along with these questions, in the book are considered processes of fuel atomization in motor and main propositions of theory of similarity of physicochemical processes.

Thus, has been made an attempt to expound main propositions which have important value for construction of an orderly theory of combustion in chamber of

liquid-fuel rocket engine in systematic form. In view of the limited volume of this book, certain questions are developed in simplified form.

This book is written on the basis of data published in the open Soviet and foreign press. Examples of structures, fuels and fuel systems presented in the book were taken from the foreign literature.

Authors express deep gratitude to associate member of Academy of Sciences of USSR Prof. A. S. Predvoditelev, who wrote Section 2 in Chapter II "Ignition of two-phase mixtures" and will be also grateful to all readers who send their remarks concerning the expounded material to this address: Moscow, I-51, Petrovka, 24, Oborongiz.

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## CHAPTER I

### ELEMENTS OF KINETICS OF CHEMICAL REACTIONS

#### Section 1. Activation Energy

Chemical kinetics, the study concerning rates of chemical reactions, is one of the divisions of physical chemistry, on which is constructed theory of combustion and propagation of flame. Combustion is first of all exothermal chemical reaction, proceeding at high temperatures. For this reason it is expedient to expound here the main positions of chemical kinetics.

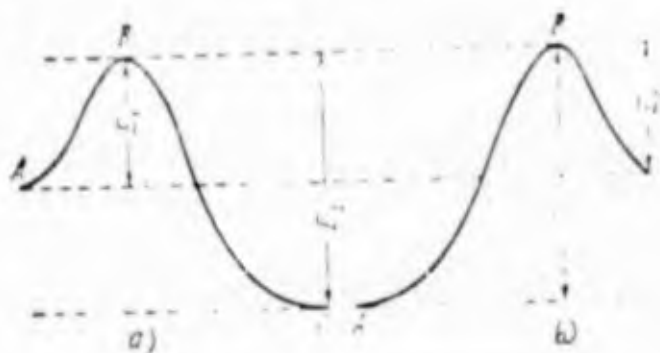


Fig. 1. Schematic representation of power barriers.  
a--exothermic reaction, b--endothermic reaction.

The main quantity characterizing the reacting ability of a molecule participating in a reaction is its activation energy in the given chemical reaction. In order to realize a chemical reaction, molecules entering into interaction must possess a minimum energy, called activation energy. This is the energy required

to weaken or destroy bond of the original molecule, after which formation of new more desired bonds is possible, leading to formation of final products of reaction.

For clarity, change of potential energy during chemical reaction can be depicted graphically (Fig. 1). In order to obtain a chemical reaction, molecules should possess a certain minimum energy  $E_1$ , which is necessary for breaking or weakening of existing bonds. By acquiring this energy and thus overcoming a certain energy barrier AB, molecules are transformed into final products (at point C) with energy release. In the case  $E_1 < E_2$  (Fig. 1, a) the total reaction energy is positive (exothermic reaction), in the case  $E_1 > E_2$  (Fig. 1, b), the reaction proceeds with absorption of heat (endothermic reaction).

Activation energy for saturated molecules is quite large and usually is equal to several tens of kilocalories. For example, for the reaction of formation of water  $E=45$  kilocalorie/mole. For reactions of saturated molecules with radicals, activation energy will be on the order of 10 kilocalories, but for reactions of atoms and radicals, it is practically equal to zero.

Increase of temperature abruptly increases the chemical reaction rate and leads to loosening or complete destruction of intramolecular bonds between atoms. Rapid increase in the rate of the chemical reaction with increase of temperature can be explained by assuming a molecular mechanism of chemical transformations. During the chaotic thermal motion, molecules of reacting gases collide with each other, but chemical reaction can occur only as a result of effective collisions.

As it is known from the molecular-kinetic theory of gases, every molecule on the average experiences  $10^{10}$  collision per sec. If upon every collision molecules reacted with each other, then any chemical reaction should occur instantly. In reality, not all collisions of molecules will lead to chemical reaction. During decomposition HI, for example, out of  $2 \cdot 10^{17}$  collisions of molecules only one collision leads to the reaction of decomposition into hydrogen and iodine. It has been proven that for practical realization of a chemical reaction, only

collision of the reacting molecules is insufficient. It is necessary that in the moment of collision the original molecules possess a definite energy, which is sufficient for weakening of bonds, which break during the reaction.

Presence of a large number of ineffective collisions is connected with the fact that for a chemical reaction is necessary collision of molecules with definite velocity and, accordingly, with definite energy. Only those collision will lead to chemical reaction, for which the energy of colliding molecules is greater than a certain minimum value of energy  $E$ . This necessary energy is the activation energy.

In the case of bimolecular reactions, activation energy is the sum of kinetic energies of the two colliding molecules. Chemical stability of molecules hampers chemical reaction.

Dependence of chemical reaction rate on temperature is expressed by the formula of Arrhenius for rate constant  $k$ :

$$k = B e^{-E/RT}, \quad (1.1)$$

where  $E$  -- activation energy;

$R$  -- universal gas constant;

$T$  -- temperature.

Quantity  $B$  characterizes total number of collisions, which is proportional to the velocity of the molecule, which in turn is proportional to  $\sqrt{T}$ :

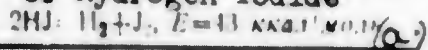
$$B = \text{const} \sqrt{T}.$$

Exponential factor in the formula of Arrhenius  $e^{-E/RT}$  from the point of view of statistical physics represents the fraction of molecules with energy larger than  $E$ . We will list values of quantity  $e^{-E/RT}$  for different temperatures (see Table 1).

Let us note that the law of Arrhenius is a particular case of the more general statistical law of Maxwell - Boltzmann, giving distribution of energy with respect to number of molecules.



Table 1. Dependence of Fraction of Active Molecules on Temperature for Reaction of Decomposition of Hydrogen Iodide



T, K	$e^{-E/RT}$
288	$6.7 \cdot 10^{-24}$
500	$7.7 \cdot 10^{-20}$
1000	$2.8 \cdot 10^{-10}$
1500	$4.2 \cdot 10^{-7}$
2000	$1.7 \cdot 10^{-5}$

KEY: (a) kcal/mole.

Taking the logarithm of the equation for

rate constant of the reaction (1.1), we obtain

$$\ln k = -\frac{E}{RT} + \ln B. \quad (1.2)$$

Since in the first approximation constant B can

be considered as not depending on temperature,

then

$$\ln k = -\frac{E}{R} \frac{1}{T} + \text{const.} \quad (1.3)$$

Constructing a graph of function  $\ln k = f(1/T)$ ,

we obtain a straight line (Fig. 2) with tangent of the angle of slope

$$\tan \alpha = -\frac{E}{R}.$$

Hence graphically can be determined the value of activation energy.

In Fig. 2 is presented as an example the graph of the dependence of  $\log k$  on  $1/T$  for the reaction of formation and decomposition of HI. Value of activation

energy can be obtained by two experimental values

of rate constant  $k_1$  and  $k_2$  at two temperatures

$T_1$  and  $T_2$ :

$$\ln k_1 = \text{const} - E/RT_1,$$

$$\ln k_2 = \text{const} - E/RT_2.$$

Eliminating the constant by subtraction, we find

$$2.3 \lg \frac{k_1}{k_2} = \frac{E}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right),$$

whence, considering  $R = 2$  kilocalories/mole,

$$E = 4.6 \lg \frac{k_1}{k_2} \frac{1}{\frac{1}{T_2} - \frac{1}{T_1}}. \quad (1.4)$$

Fig. 2. Dependence of  $\log K$  on  $1/T$  for reaction of formation and decomposition of hydrogen iodide.

KEY: (a) kcal/mole; (b)  $\log (k \cdot 10^9)$ .

According to the empirical rule of Eyring [1] for the reaction of two diatomic molecules



Value of activation energy

$$E = \frac{1}{4} (D_{AB} + D_{CD}). \quad (1.5)$$

where  $D_{AB}$  and  $D_{CD}$  are energies of dissociation of respective molecules (see Table 2).

Table 2. Energy of Dissociation of Diatomic Gases [183]

Молекула (a)	Энергия диссоциации ккал/моль (b)	Молекула (a)	Энергия диссоциации ккал/моль (b)
H <sub>2</sub>	103,242	N <sub>2</sub>	225,1
O <sub>2</sub>	117,946	HCl	102,104
C <sub>2</sub>	57,080	HBr	86,577
F <sub>2</sub>	37,000	I <sub>2</sub>	70,487
OH	103,0	BeO	121,652
CO	256,189	BO	175,0
NH	85,000	BcH	53,000
NO	150,0	LiH	57,700
SiN	101,000	AlO	133,500
HF	134,00	BF	196,000

KEY: (a) Molecule; (b) Energy of dissociation kilocalories/mole.

Zel'dovich and Vovayevodskiy [2] indicate that activation energy of an endothermic reaction can be determined as the sum of reaction energy and the activation energy of the reverse exothermic reaction.

Table 3. Theoretical and Experimental Values of Activation Energy [1]

Реакция (a)	Значение энергии активации $E$ ккал/моль (b)	
	эксперимен- тальное (c)	рассчитанное (d)
H <sub>2</sub> + J <sub>2</sub> = 2HJ	40	40
H <sub>2</sub> + Br <sub>2</sub> = 2HBr	> 43	43
H <sub>2</sub> + JCl = HJ + HCl	> 34	42

KEY: (a) Reaction; (b) Value of activation energy kilocalories/mole; (c) experimental; (d) theoretical.

Experimental values of activation energy for reactions of molecules of halogens and hydrogen are satisfactorily coordinated with data calculated by the empirical rule of Eyring (see Table 3).



## Section 2. Monomolecular Reactions

Chemical transformations in which only one original substance is subjected to change, i.e., there occurs spontaneous decomposition of the substance without participation of a second component, are called monomolecular. Examples of such reactions are the following:

decomposition of nitrogen pentoxide\*



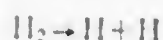
decomposition of nitrous oxide



decomposition of acetone



dissociation of hydrogen



and other reactions.

Example of monomolecular reactions is also spontaneous decay of radioactive substances, occurring without external influence. In this type of reaction it is possible to include also photochemical disintegration under action of light. In general, the number of monomolecular reactions is relatively small.

Let there be  $a$  moles of original substance, from which during the time  $t$ ,  $x$  moles react; consequently,  $(a-x)$  moles remain unreacted. Then the rate of reaction

$$\frac{dx}{dt} = k(a-x).$$

By separating variable we obtain

$$\frac{dx}{a-x} = k dt$$

---

\* There is written the equation of total reaction. In reality, monomolecular decomposition goes by the scheme  $\text{N}_2\text{O}_5 \rightarrow \text{NO}_3 + \text{NO}_2$  and is accompanied by the bimolecular process  $\text{NO}_3 + \text{NO}_2 = \text{NO}_2 + \text{NO} + \text{O}_2$ . (Ed. note).

and after integration

$$-\ln(a-x) = kt + C, \quad (1.6)$$

where C -- constant of integration.

Using initial condition  $x=0$  at  $t=0$ , we find  $C=-\ln a$  after which instead of (1.6) we have

$$-\ln(a-x) = kt - \ln a,$$

whence

$$k = \frac{1}{t} \ln \frac{a}{a-x}. \quad (1.7)$$

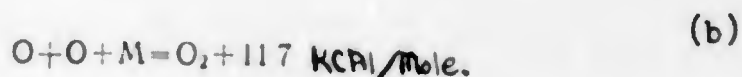
As an example, let us consider in more detail the reaction of decomposition of nitrous oxide  $N_2O$ . Reaction proceeds with release of heat by the equation



Molecule  $N_2O$  acquires energy due to redistribution of energy during collisions with other molecules:



Reaction of decomposition of excited molecules occurs in stages:\*



Large endothermicity of reaction (a) requires great activation energy, which is equal to 53 kilocalories/mole.

Reaction of decomposition of  $N_2O^*$  is monomolecular. Excited molecule of nitrous oxide possesses necessary energy for breaking of one of its chemical bonds and does not require collisions similarly to bi- and trimolecular reactions. Excited molecule  $N_2O^*$  has definite probability of decomposition into atom O and

---

\*Mechanism of reaction of thermal decomposition of nitrous oxide is considered in simplified form. (Ed. note).

molecule  $N_2$ . This probability is characterized by mean life of excited molecule  $\tau^*$  or rate constant

$$k = 1/\tau^*.$$

Distinction of this process consists in that disintegration of  $N_2O^*$  occurs neither under the influence of any other molecules, nor during collision, but during free motion of molecule, as a result of processes occurring inside one molecule.

Chemical reaction rate is proportional to concentration of excited -- rich in energy -- molecules of nitrous oxide  $N_2O^*$ . Rate of formation of these molecules can be expressed by the formula

$$u = Z_{N_2O \cdot M} e^{-53000/RT}. \quad (1.8)$$

where  $Z_{N_2O \cdot M}$  -- total number of collisions of  $N_2O$  with any molecule of the system. In the given case, collision of excited molecule with any other can lead to the case when the excited molecule, giving off excess energy, will be transformed into an ordinary molecule.

During course of reaction, automatically, in a very short time (many times less than time of reaction), there is established the so-called steady state, in which rate of formation of active molecules equals sum of rates of reactions of decomposition of  $N_2O^*$  into free nitrogen and oxygen and rate of deactivation, i.e., number of collisions experienced by these active molecules.

Rate of reaction under the conditions when disintegration of excited molecules only slightly changes their concentration as compared to equilibrium, concentration can be expressed by the following formula:

$$u = \frac{1}{\tau^*} e^{-53000/RT} n, \quad (1.9)$$

where  $\tau^*$  -- lifetime of excited molecule;

$e^{-53000/RT} n$  -- number of excited molecules.

For other monomolecular reactions of decomposition of polyatomic molecules, lifetime of excited molecules is one-two orders larger.

Reaction of decomposition of nitrous oxide at temperature of 900 degrees C on surface of gold was studied by Hinshelwood. His experimental data (see Table 4) confirm monomolecular nature of reaction of decomposition of nitrous oxide.

Table 4. Decomposition Rate of  $N_2O$  at 900° C

Time t (a)	x %	k
900	16,5	0,00016
1800	32,0	0,00016
3150	50,0	0,00016
5000	57,0	0,00016
4800	65,0	0,00016
6000	73,0	0,00016
7200	78,0	0,00016

KEY: (a) Time in sec.

If by the moment of time t disappears x % of the  $N_2O$ , then according to (1.7)

$$\text{rate constant of reaction } k = \frac{1}{t} \ln \frac{100}{100-x}$$

Placing in this equation values of x for various moments of time t, we obtain value of rate constant of chemical reaction which is k constant on the average, which indicates monomolecular nature of the considered reaction.

### Section 3. Bimolecular Reactions

Majority of reactions realized in practice are bimolecular. So that a bimolecular reaction occurs, it is necessary for a collision of two particles (atoms, radicals or molecules) to occur. Let there be taken two substances in equimolecular quantities. Let, further, at moment of time t, from moles of each substance present in the beginning react x moles; then, considering that rate of reaction is proportional to product of concentrations, we can write

$$\frac{dx}{dt} = k(a-x)(a-x) = k(a-x)^2 \quad (1.10)$$

After separation of variables and integration we obtain

$$\frac{1}{a-x} = kt + C \quad (1.11)$$

Considering that  $x=0$  at  $t=0$ , we find constant of integration

$$C = \frac{1}{a}$$

Placing value C into the equation (1.11), after transformations we finally obtain the formula

$$k = \frac{1}{t} \frac{x}{a(a-x)}$$

Cases are possible when original substances are taken in nonequivalent quantities. We assume that at initial moment of time, quantity of one of components equals  $a$  moles and the other --  $b$  moles. Let by moment of time  $t$  there react  $x$  moles each of each component; then, rate of bimolecular reaction

$$\frac{dx}{dt} = k(a-x)(b-x). \quad (1.12)$$

Separating variables and producing integration, we obtain

$$k = \frac{1}{t} \frac{1}{a-b} [\ln(a-x) - \ln(b-x)] + C. \quad (1.13)$$

Using initial condition  $x=0$  at  $t=0$ , we find

$$C = \frac{1}{a-b} (\ln b - \ln a).$$

Placing expression  $C$  into the equation (1.13), finally we obtain

$$k = \frac{1}{t} \frac{1}{a-b} \ln \frac{b(a-x)}{a(b-x)}. \quad (1.14)$$

As one of examples of bimolecular reactions can serve reaction of hydrogen with iodine, which proceed according to equation.



Rate of this reaction

$$v = -\frac{dc_{\text{H}_2}}{dt} = -\frac{dc_{\text{I}_2}}{dt} = \frac{1}{2} \frac{dc_{\text{HI}}}{dt} = k c_{\text{H}_2} c_{\text{I}_2}. \quad (1.15)$$

This formula agrees well with experimental data on dependence of rate of reaction on time. Thus, it is unimportant whether or not we change the concentration of hydrogen or iodine vapor from without, taking for experiment one or another quantity of reacting substances, or whether or not concentration of hydrogen and iodine is attained in process of reaction, as a result of decrease of initially taken large concentration of one of the original substances.

Rate constant of reaction

$$k = B_{\text{H}_2\text{I}_2} e^{-E/RT},$$

and here

$$B_{\text{H}_2\text{I}_2} c_{\text{H}_2} = Z_{\text{H}_2\text{I}_2},$$

where  $Z_{\text{H}_2\text{I}_2}$  -- total number of collisions of molecules of hydrogen with molecules

of iodine per unit of time.

Calculation of the time which is necessary so that one percent of mixture  $H_2 + I_2$  reacts was performed by Zeldovich and Voyevodskiy [2]. According to this calculation these times are equal to years,

at 273° K -- nearly  $10^{14}$  years,

at 600° K -- nearly 0.5 hours,

at 800° K -- nearly 1 sec.

Considered example indicates sharp dependence of chemical reaction rate on temperature. Increase of absolute temperature by two times appears sufficient for increase of rate of reaction by  $10^{16}$  times.

#### Section 4. Recombination of Atoms and Radicals

Reactions of atoms and radicals, i.e., active fragments with unsaturated valences, are different from ordinary molecular reactions. While for realization of reactions between molecules it is necessary to expend a definite energy for breaking of bonds, for atomic and radical reactions activation energy is very insignificant.

Phenomena of recombination of atoms of hydrogen frequently have been discussed in scientific and technical literature. There was indicated, in particular, the fact that hydrogen atoms capable of recombining are an ideal fuel, especially in those cases when it is necessary to have a maximum store of energy with minimum weight, for example during interplanetary journeys with the help of rockets. We will see whether or not there are possibilities to use atomic hydrogen as rocket fuel, and if it is possible for a sufficiently long time to store this fuel and use it as the need arises. In the case of interaction of two hydrogen atoms, with formation of a molecule of hydrogen, activation energy equals zero.

Rate of reaction of recombination  $A+B \rightarrow AB$  is expressed by the formula

$$\frac{dc_{AB}}{dt} = k_1 k_2 c_A c_B c_N. \quad (1.16)$$



where  $k_1$  — rate constant formation of a quasimolecule (molecule with surplus of energy);

$k_2$  — rate of process of stabilization;

$c_n$  — concentration of third body;

$\tau$  — average duration of existence of complex.

In 1928 N. N. Semenov [3] showed that if excited atom collides with a normal one, surplus of energy is radiated at the moment of impact, during formation of an electronically unexcited molecule. Such recombination occurs during burning of hydrogen halides.

However, it is necessary to remark that not every simple collision between two atoms of hydrogen leads to formation of a stable molecule of hydrogen. Hydrogen molecules with supply of energy larger than binding energy of molecule, immediately after formation are destroyed. Stabilization is realized by the method of "triple impact"; as a third body can serve an atom, molecule or wall of vessel. For formation of a stable hydrogen molecule, there is necessary during collision of two atoms of hydrogen the presence of a third particle, which during recombination is the receiver of excess energy of the molecule of hydrogen. Thus, there is obtained a stable molecule of hydrogen. Energy remaining in the molecule of hydrogen is insufficient for its destruction. All which has been said above is observed during any reactions of recombination. If during the life time of the excited, rich in energy, molecule, it does not have time to give up its energy to some third particle or the wall, then the molecule again breaks up into atoms.

In order to form a hydrogen molecule as a result of collision between two atoms of hydrogen, there is required a triple collision according to the scheme



where M — particle, receiving the excess energy during recombination.

Triple collision can be considered as a double collision occurring in a place where there is a third particle M. Probability of triple collisions is much less

than that of double collisions. For this reason experimental magnitude of rate of reaction is considerably less than number of double collisions.

Zel'dovich and Voevodskiy [2] showed that time of recombination of atoms of hydrogen into a molecule equals  $23 \cdot 10^{-6}$  sec. Their calculation shows that in practice, recombination of atoms of hydrogen into a molecule occurs instantaneously and use of hydrogen atoms as fuel is impossible if there are no methods of conservation of atomic hydrogen, and it is impossible to expend it only when needed.

Only known method of stabilization and conservation of free radicals is freezing them in the solid phase at a temperature near to absolute zero. If this is the only possible way, then in motors of the future it is possible to expect use of fuel in the form of rods, at extraordinarily low temperature. Rods can be in the appropriate way isolated, and during heating of one end, free radicals will recombine with energy release.

At present the problem of obtaining, storage and use of free radicals (H, NH, OH et al.) as high energy fuels for rocket motors has become the object of wide investigations [4].

#### Section 5. Chain Reactions

In 1912 Einstein established the main law of photochemistry, according to which the number of primary events of a photochemical reaction must be equal to the number of absorbed quanta of light, or every absorbed quantum of radiation causes one elementary event of chemical transformation



During experimental verification of the new law, it turned out that a number of photochemical reactions indeed strictly obey it. However, already in 1913, Bodenstein showed that quantum yield (number of moles of substance undergoing transformation during absorption of one mole of quanta) of different photochemical reactions are spread from 0.002 to  $10^6$ . These deviations from law of Einstein

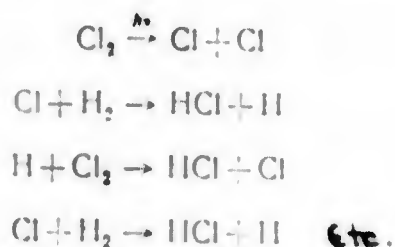


caused necessity for explanation of anomalously high quantum yields, which served as an impetus for new theoretical investigations and led to development of concepts of chain mechanism of chemical reactions.

Theory of chain reactions received main development in classical investigations of academician Semenov and his school (Kondrat'ev, Koval'skiy, Emanuel', Voyevodskiy, Nalbandyan, et al.).

### 1. Non-Branching Chain Reactions

A clear example of this type of reactions is the reaction of a compound of chlorine with hydrogen. Formation of HCl occurs in a chain reaction -- successive alternation of reactions of atomic chlorine and hydrogen, regenerating one another. A molecule of chlorine under the action of light or temperature easily dissociates into atoms. Atom of chlorine with molecule of hydrogen will form hydrogen chloride with liberation of atomic hydrogen, which then reacts with a molecule of chlorine



Reaction  $\text{Cl} + \text{H}_2 \rightarrow \text{HCl} + \text{H}$  requires small activation energy, equal to 6 kilocalories/mole. Atomic hydrogen chemically is more active, and reaction of interaction  $\text{H} + \text{Cl}_2 \rightarrow \text{HCl} + \text{Cl}$  requires still lower activation energy (2 kilocalories/mole). In the given case there is obtained a chain of reactions, continued by turn by active centers -- atoms of hydrogen and chlorine.

Thus, the active center as a result of interaction with another particle will form a reaction product, as well as a new active particle, which in the future course of the chemical reaction continues the chain until the destruction of the active center itself, or to so-called termination of the chain. Termination of

the chain can occur as a result of recombination of active particles in the volume or on the wall. For non-branched chain reactions constancy of concentration of active centers is characteristic, since as many centers as are formed will enter into reaction. For this reason, rate of non-branched chain reactions does not exceed a limiting value.

Reaction of formation of atoms of chlorine can be represented by equation



reaction of recombination of atoms of chlorine during triple collision with particle M in molecule of chlorine -- by equation



At first glance it may appear that recombination of atoms of chlorine and hydrogen can occur during simple formation of atoms into a molecule according to the scheme  $\text{H} + \text{H} \rightarrow \text{H}_2$  and  $\text{Cl} + \text{Cl} \rightarrow \text{Cl}_2$ . Actually such recombination has small grounds. In reality, as was already indicated above, not every collision of two atoms leads to formation of a stable molecule, in view of formation of molecules rich in energy, in which the supply of energy is larger than binding energy.

Designating rate constants of formation of atoms of chlorine by  $k'_1$ , it is possible to write the equation

$$k_1 c_{\text{Cl}_2} c_M = k'_1 c_{\text{Cl}}^2 c_M \quad (1.17)$$

hence the concentration of atoms of chlorine

$$c_{\text{Cl}} = \sqrt{\frac{k_1}{k'_1} c_{\text{Cl}_2}} \quad (1.18)$$

Rate of formation of hydrogen chloride equals sum of rates of two reactions



Since atomic hydrogen formed during reaction (a) enters into reaction with chlorine by reaction (b), the quantities of HCl that will be formed during every reaction are equal. As a result of rate of formation of hydrogen chloride

$$u = \frac{dc_{\text{HCl}}}{dt} = 2k_2 c_{\text{Cl}} c_{\text{H}_2}. \quad (1.19)$$

Placing into this formula the expression for  $C_{Cl}$  by (1.18), we obtain

$$u = 2k_2 \sqrt{\frac{k_1}{k_3}} c_{Cl_2} c_{H_2} \quad (1.20)$$

In this formula square root of concentration of original substance points out the role of atoms in the reaction. From formula (1.20) it follows that reaction of formation of hydrogen chloride is of order one half with respect to chlorine.

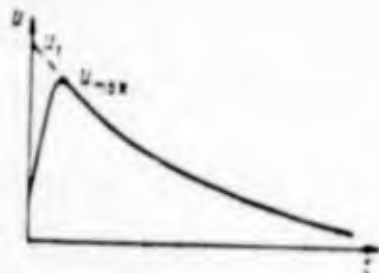


Fig. 3. Character of flow of non-branched chain reaction with time.

Chain reaction of formation of HCl proceeds  $10^5$  times as fast as an ordinary bimolecular reaction. Character of flow of non-branched chain reaction at constant temperature is shown graphically in Fig. 3. If mixture of hydrogen and chlorine is at constant temperature, then with decrease of con-

centration of reacting substances, rate of reaction will be decreased in accordance with (1.20).

From Fig. 3 it is clear that in the beginning, rate of reaction increases to maximum possible  $u_{max}$  at given temperature, but then is decreased, approaching zero. Increase of rate of reaction is connected with increase of concentration of active centers, atoms of chlorine and hydrogen, but decrease of rate is connected with termination of chains occurring as a result of recombination of active particles in the volume, or on the wall, or during their interaction. Curve  $u_1$  corresponds to behavior of simple chemical reaction.

## 2. Branched Chain Reactions

A very interesting and the most studied example of branched chain reactions is reaction of burning of hydrogen. Nusselt [5], investigating propagation of flame in explosive mixtures, considered that reaction of combination of hydrogen with oxygen occurs in one event, during collision of two molecules of hydrogen and one molecule of oxygen, exactly according to the stoichiometric equation of the

reaction



Based on this assumption, he considered that rate of reaction

$$v = kc_{\text{H}_2}^2 \cdot c_{\text{O}_2}. \quad (1.22)$$

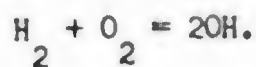
In reality, kinetics of actual process does not have anything in common with equation (1.22). Indeed, according to equation (1.22), rate of reaction should gradually diminish in time because of decreases of concentrations of original substances. However, experimental data indicate strong increase of rate of reaction with development of the process.

Thanks to the numerous works of Semenov and his pupils, and also many foreign scientists, the mechanism of this reaction was established by experimental works and confirmed by theoretical calculations. As distinguished from non-branched chain reactions, during burning of hydrogen the reaction proceeds by a branched chain mechanism, which leads to autoacceleration and explosion.

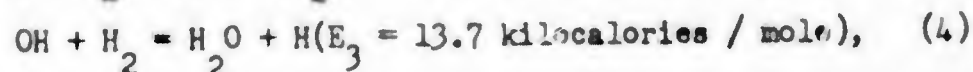
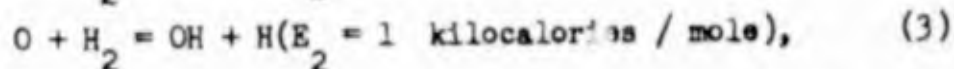
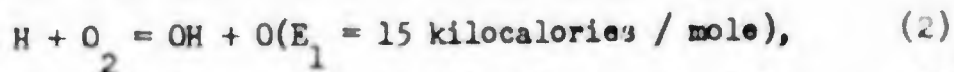
First event by chain reaction is creation of active center (atom or radical) from stable molecule. In the case of reaction of oxidation of hydrogen, first event is disintegration of molecule of hydrogen into atoms of hydrogen — carriers of the chain.



Possible also is the process

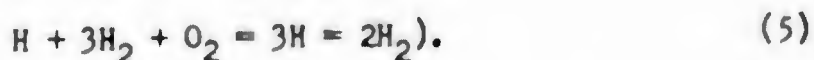


First event (1) serves as the start of the chain reaction



Reactions (3) and (4) have lower energies of activation and proceed faster than reaction (2), and total rate of process is determined by rate of reaction (2).

Total equation of chain



From equations (2), (3), (1) and (5) it is clear that atom of hydrogen starting the chain reaction, again is regenerated in the course of the chain process, and one atom of hydrogen entering into reaction (2) causes creation of three atoms. In other words, chain is branched and there are created conditions for formation of an avalanche of active centers.

Progressive increase of number of active centers and increase of rate of reaction will lead to self-ignition, if termination of chain does not interfere with course of process.

Scheme of development branched chain of reactions

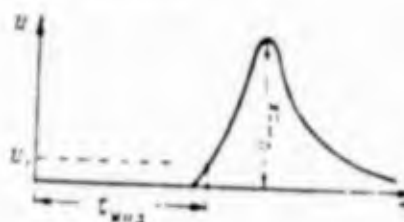
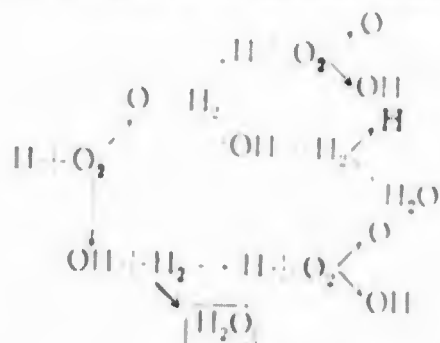


Fig. 4. Rate of branched chain reaction.

Complicated mechanism of chain combustion of hydrogen can be considered at present to be fully confirmed by numerous experimental data. The most convincing are results of direct measurement of concentrations of atoms of hydrogen and radicals of hydroxyl in the flame.

For first stage of development of chain reaction, when concentrations of hydrogen atoms are not very great, and it is possible to disregard secondary reactions of termination of chains as well as initiation of chains, rate of reaction according to Zel'dovich is

$$u = \frac{dc_{H_2O}}{dt} = \frac{dc_H}{dt} = 2k_2 c_H c_O = 10^{11} \sqrt{T} e^{-\frac{15000}{T}} c_H^2 c_{O_2} \quad (1.23)$$

At the beginning of development of reaction, its rate can be considered to be proportional to the concentration of atomic hydrogen  $\frac{dc_H}{dt} \sim c_H$

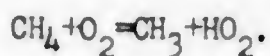
Reaction proceeds strong autoacceleration. For reaction, proceeding according to the scheme of chain branching, presence of period of induction  $\tau_{ind}$  is

characteristic during which there occurs build-up of concentration of hydrogen atoms. Change of rate of reaction with chain branching in time is schematically depicted in Fig. 4.

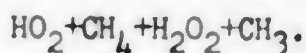
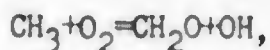
Flow of reaction with branched chains completely is determined by concentration of active centers--atoms of hydrogen. If initial concentration of atoms of hydrogen in system is increased, then period of induction will be reduced and reaction will proceed with high rate; conversely, if we remove from the reactionary volume hydrogen atoms, the reaction will be retarded and period of induction will be increased. During intense recombination of atoms of hydrogen into molecules, chain self-ignition in general will not occur.

### 3. Chain Reactions With Degenerate Branchings

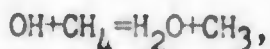
Semenov [18] showed that there are cases when chain branchings occur not as a result of interaction of active center with molecule of original substance, but as a result of disintegration of molecules of intermediate products into radicals. In such a case the time of autoacceleration is determined by the rate of formation of primary radicals from these molecules. Semenov called this type of chain reactions "degenerate chain explosions", and branching due to intermediate comparatively stable products--degenerate branchings. Example of such reactions is oxidation of hydrocarbons and, in particular, methane with molecule of oxygen leads to formation of two radicals



Each of these radicals can give a new radical



Hydroxyl can react with methane

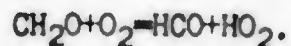


as well as with aldehyde

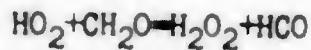
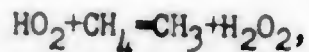
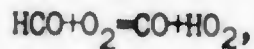




Aldehyde can be oxidised by reaction of degenerate branching



Each of formed radicals reacts to form new radicals:



Thus, intermediate product--aldehyde--not only reacts to form final products, but also can give active centers--radicals, increase of concentration of which accelerates the reaction on the whole.

### Section 6. Chain Self-ignition

In the classical monograph of Semenov [18] were established main concepts and mechanisms of chain and thermal ignitions, which served as a basis for intense development of the contemporary of combustion and explosion.

From usual chemical reactions, explosive reactions are distinguished by the rate of chemical transformation and its change in time. Dependence of rate of reaction on temperature near to the temperature of ignition is insignificant and practically imperceptible. When the temperature of the mixture is raised to the temperature of ignition, there occurs an instantaneous flash, and the reaction is carried out in thousandths of a second. From this it follows that for explosive reactions is characteristic a sharp build-up of rate of reaction.

For majority of chemical reactions proceeding with an explosion, the mechanism is chain reaction. Rate of process is proportional to concentration of active centers carrying out the process.

Dependence of concentration of active centers on time is expressed by following equation:

$$\frac{dn}{dt} = W_0 + fn - gn, \quad (1.24)$$

where  $W_0$  -- rate of formation of active centers;

$f$  -- rate constant of branching of chain;

$g$  -- rate constant of termination of chain;

Introducing designation  $f - g = \varphi$ , formula (1.24) can be rewritten in this form:

$$\frac{dn}{dt} = W_0 + \varphi n. \quad (1.25)$$

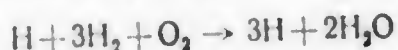
Integrating equation (1.25) for initial condition  $n = 0$ , we obtain following expression for actual concentration of active centers

$$n = \frac{W_0}{\varphi} (e^{\varphi t} - 1). \quad (1.26)$$

Rate of chain reaction, i.e., rate of formation of final products, is described by equation of Semenov

$$W = \frac{aW_0}{\varphi} (e^{\varphi t} - 1). \quad (1.27)$$

In the equation (1.27), factor  $a$  represents number of molecules of final products of reactions formed due to entry into the reaction of every active center. For reaction of combustion of hydrogen according to the empirical equation



factor  $a = 2$  since reaction of one atom of hydrogen leads to formation of two molecules of water.

Dependence of rate constant of actual branching of chains  $\varphi$  on pressure and temperature can be represented by the following equation, validity of which Semenov and his collaborators experimental confirmed [18]:

$$\varphi = CP^m e^{\frac{\gamma}{T}}, \quad (1.28)$$

Where  $C$ ,  $m$ ,  $\gamma$  -- constants.

Occurrence of the reaction depends on relation between rates of branching and termination of chains, i.e., the sign of constant  $\varphi$ . With increase of temperature, quantity  $\varphi$  changes sign from negative to positive. At  $\varphi < 0$  rate of formation of active centers decreases with time, but at  $\varphi > 0$  rate of formation of active centers increases, i.e., branching of chains occurs faster than termination and reaction autoaccelerates and grows without limit by an exponential law. The greater the difference  $f - g = \varphi$  the faster increases the rate. Temperature, at



which  $\varphi = 0$  corresponds to critical temperature, below this temperature chain explosion is impossible. Character of course of the reaction at different magnitude  $\varphi$  is shown in Fig. 5.

During explosive reactions proceeding by mechanism of chain branching, rate of formation of initial active centers  $u_0$  is considerably less than the smallest rate of reaction  $u_1$  which is subject to observation. In this case the corresponding period of induction has magnitude  $\tau_{ind}$  considerably larger than unity. On this basis, the formula of Semenov can be simplified and with sufficient accuracy represented in the form

$$W = \frac{a/W_0}{\varphi} e^{\varphi \tau_{ind} u_0} \quad (1.29)$$

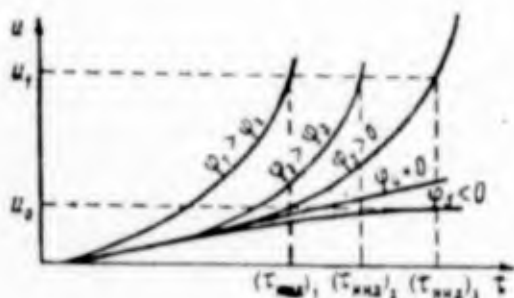


Fig. 5. Course of the reaction at different values of  $\varphi$ .

At large values of  $\varphi$ , i.e., when  $f \gg g$ ,

$$W_1 = W_0 e^{\varphi \tau_{ind} u_0},$$

whence there can be easily obtained the expression for period of induction:

$$\tau_{ind} = \frac{1}{\varphi} \ln \frac{W_1}{a/W_0}.$$

Dependence  $\tau_{ind}$  on  $W_0$  and  $a$  is weak, since they are under the sign of the logarithm.

Thus,

$$\tau_{ind} = \frac{\text{const}}{\varphi}. \quad (1.30)$$

During the period of induction (delay of ignition) chemical reaction goes slowly, with a rate which is not subject to determination, and the concentration of active centers continuously increases.

## Section 7. Thermal Self-ignition

Qualitative picture of thermal explosion was given by Vant-Goff [6], but quantitative theory, for the first time formulated by Semenov [18], received further development in works of his pupil Todes [7] and Frank-Kamenetskiy [8].

Assuming the idea of a slowly proceeding exothermal reaction, Semenov gave mathematical formulation of conditions of transition from stable rate of reaction

to progressively increasing rate, corresponding to the condition of occurrence explosion. Essence of theory consists in the fact that heat of exothermal reaction does not have time to be given off to the medium (walls of vessel), and heats the gas. Due to such heating, chemical reaction is accelerated by exponential (relative to temperature) law and there occurs constantly increasing self-heating of mixture, leading to unlimited autoacceleration, which end in a thermal explosion.

Let us consider chemical reaction in gas mixture, proceeding in a vessel. Let wall of vessel and gas mixture at initial moment of time have temperature  $T$  and pressure  $p$ . In the course of chemical reaction, temperature of mixture changes. According to the law of Arrhenius, this change of temperature effects rate of reaction

$$u = Bp^n e^{-E/RT}, \quad (1.31)$$

where  $B$  — a constant, depending on composition of mixture;

$n$  — small integer or fraction, determining effective order of reaction.

Rate of heat release for reacting system

$$\Phi_1 = Q^*u. \quad (1.32)$$

where  $u$  — rate of reaction

$Q^*$  — reaction energy in kilocalories/mole

Placing expression for  $u$  in (1.32), we obtain

$$\Phi_1 = Q^*Bp^n e^{-E/RT}. \quad (1.33)$$

Since cooling is realized by heat transfer out of zone of reaction to walls of vessel, quantity of heat lost through walls of vessel per unit of time equals

$$\Phi_2 = \alpha (T - T_0) \frac{S}{V}. \quad (1.34)$$

where  $\alpha$  — heat-transfer coefficient;

$S$  — surface of vessel

$V$  — volume of vessel;

$T_0$  -- initial temperature of walls of vessel;

$T$  -- temperature of zone of reaction.

In Fig. 6 is presented dependence of quantities  $\Phi_1$  and  $\Phi_2$  on temperature. Rate of heat release  $\Phi_1$  during increase of temperature, increases by exponential law, and rate of cooling  $\Phi_2$  by linear law.

It is natural that at a temperature of fuel mixture equal to the temperature of walls of vessel, there is no heat loss, but with flow of the chemical reaction there will be released heat and the increase of temperature will create a difference of temperatures  $T - T_0$ .

At some temperature  $T_1$  rate of heat transfer becomes equal to rate of heat release in reacting volume. Then further increase of temperature and, consequently, of the chemical reaction rate is stopped. If temperature of reacting gas is less than  $T_3$  (see Fig. 7), then rate of cooling will be larger than rate of heat release and temperature will be lowered to value  $T_1$ . Conversely, if gas is preheated to value  $T > T_3$ , then heat release abruptly will increase -- there will occur ignition.

The higher the pressure and concentration of fuel mixture in vessel, the higher at constant temperature  $T_0$  is the rate of reaction, and accordingly of the heat release in the reacting volume. Since rate of cooling does not depend on pressure then at small pressures heat release cannot be greater than cooling, and, consequently, chemical reaction will proceed at temperatures near to temperature of vessel. With increase of pressure, rate of heat release increases, but cooling at every given difference of temperatures remains constant. It is natural that for given temperature there exists minimum of pressure, at which  $\Phi_1 = \Phi_2$ . At higher pressure, when  $\Phi_1 > \Phi_2$ , rate of reaction in accordance with increase of temperature increases and there occurs explosion. Rate of reaction with increase of temperature increases continuously, and ignition is the result of the fact that, starting from a definite value of temperature rate of cooling is insufficient to

compensate for the rate of heat release.

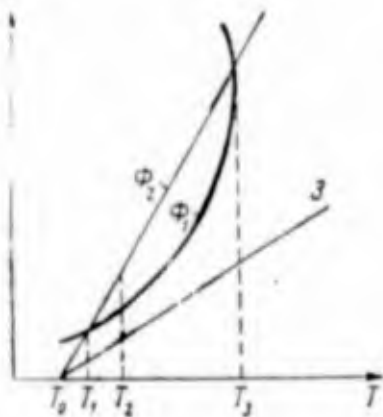


Fig. 6. Dependence of quantities  $\phi_1$  and  $\phi_2$  on temperature.

Such a mechanism of ignition is due to purely thermal causes. In the preceding paragraph we considered the possibility of analogous avalanche - like acceleration of a chemical reaction, caused in reacting system by active centers. In reality self-ignition of fuel mixtures has a combined character. Increase of chemical reaction rate, heat release and concentration of active centers with increase of temperature pro-

ceed parallel to each other and are interrelated.

## CHAPTER II

### HOMOGENEOUS AND HETEROGENOUS COMBUSTION

Combustion of fuel in different technical apparatuses occurs under complicated hydrodynamic conditions; therefore, establishment of mechanisms of transformation of fuel mixtures which proceed at high temperatures presents large difficulties. It is necessary to explain the basic mechanisms of uncomplicated normal combustion, which are an initial prerequisite for establishment of laws governing furnace processes, for establishment of maximum regimes and conditions of forcing, which have great practical value.

In spite of the fact that phenomenon of propagation of flame have been completely correctly described, attempts to construct an accurate quantitative theory of normal burning have been unsuccessful.

Main disadvantage of old theories is then use of concept of temperature of ignition as a physicochemical constant. According to these theories, a fresh fuel mixture approaching the zone of combustion is warmed up by heat released from this zone to  $T_g$ , after which there occurs ignition and the mixture violently burns with constant rate until it burns up. At the end of combustion, temperature will attain its maximum value. These conceptions, in various forms, were repeated in theories of Jouguet [9], Nusselt [5], Daniell [10], etc.

By investigations of Semenov [11], Frank-Kamenetskiy [6] and Todes [7] it was established ignition temperature not a physicochemical constant of the fuel mixture, but depends on parameters of the mixture (composition, pressure) and apparatus

conditions (conditions of heat transfer). Regarding the idea concerning constancy of reaction rate in the range of temperatures from  $T_B$  to  $T_{max}$ , this assertion contradicts the exponential dependence of increase of chemical reaction rate on increase of temperature. It is known that reaction rate at temperature of ignition is still insignificant, but after it there will be created necessary conditions of progressive autoacceleration, and reaction proceeds at temperatures of combustion.

Before the appearance of works of Lewis and Elbe and Zel'dovich and Frank-Kamenetskiy, many authors used the concept of temperature of ignition.

A correct theory of normal combustion should connect speed of flame with terminal rate chemical reaction in zone of combustion. It is necessary to consider that rate of reaction is not constant, but depends on temperature and composition, which strongly change within a narrow zone which represents the front of the flame. Also it is necessary to consider that in zone of reaction, besides heat transfer, there exist also diffusion flows of initial substances and combustion products, having opposite directions. Consequently, theory should consider heat transfer, as well as process of diffusion in flame.

This problem, formulated by Lewis and Elbe [12], for the first time was solved by Zel'dovich and Frank-Kamenetskiy [13], [14], who formulated all the main conclusions of contemporary theory of normal combustion. Lewis and Elbe, omitting the conception concerning temperature of ignition, and introducing expressions for rate of reaction as a function of temperature and concentration, consider the influence of the process of diffusion and thermal conduction, applying thus the equations of continuity. The authors assume that active atoms and radicals of the flame diffuse into the fresh gas and play an important role in preparation of fresh gas for reaction. Then this theory was refined and developed in detail in works of Zel'dovich.

In later years has appeared theory of normal combustion of Hirschfelder, Curtiss, and their collaborators [15], [16]. These authors proceeded in essence from the



same premises as Zel'dovich and Frank-Kamenetskiy, constructing equation of mass and energy balance in the front of the flame and considering the influence of reactions proceeding in the flame.

For finding speed of flame, they reject the method of some kind of simplification upon integration of system of nonlinear differential equations describing processes of diffusion and thermal conduction in the front of the flame. Authors instead presume to find exact solution by means of numerical integration of these equations with use of all the wide possibilities of contemporary calculating technology.

In the article of Evans [17] there was made a detailed survey of theories of normal combustion and there were considered in detail the original premises of different authors.

Predvoditelev considers front of flame as surface of discontinuity of parameters of system (rates of chemical reactions, density, temperature, etc.) and investigates the speed of displacement of such a discontinuity. Results obtained in these investigations make a serious contribution to the theory of normal propagation of flame.

#### Section 1. Theory of Normal Speed of Flame of Zel'dovich and Frank-Kamenetskiy

As was noted above, in attempts to construct a theory of normal speed of flame along with the main value of factor of thermal conduction connected with consecutive heating of fuel explosive mixture by heat emanating during the reaction, there was added the essential value of temperature of ignition of the mixture. It was considered that at temperatures lower than the temperature of ignition chemical reaction rate equals zero, but at the temperature of ignition it will in a jump attain an extraordinarily large magnitude. From the point of view of the contemporary theory of ignition, chemical reaction rate does not at all undergo a jump at the temperature of ignition, and depends not only on properties of the explosive mixture, but also on size and forms of vessels in which it is measured.

Zel'dovich and Frank-Kamenetskiy, creating theory of normal speed of propagation of flame, consider that a rational theory should express speed of propagation of flame in mixture, in which chemical reaction rate is given as function of temperature and concentration of reacting substances.

Propagation of flame is result of transfer of heat released in flame from hot gas mixture to still unburned gas. Inasmuch as thermal conduction plays large role in propagation of flame, for establishment of law of propagation it is necessary to construct equation of thermal conduction in burning gas. It is necessary also to consider change of concentration of reacting components from maximum value in original mixture to zero in reaction products, find connection between temperature and concentration in flame and consider dependence of rate of release of heat in flame on concentration. These considerations lead to necessity of simultaneous solution of equations of thermal conduction and diffusion.

According to what was expounded above, for description of propagation of flame in space there is required introduction to the theory, which does not use conception of temperature of ignition, principles of phenomena of transfer. Constants of a substance which characterize transfer, are diffusion coefficient and thermal conductivity.

Dimensions of diffusion coefficient (D) are  $\text{cm}^2 / \text{sec}$ . Ratio of thermal conductivity to volume heat capacity of medium gives a quantity called thermal diffusivity:

$$\frac{\lambda}{c_p} \quad [\text{cm}^2/\text{sec}], \quad (2.1)$$

where  $\lambda$  -- thermal conductivity;

$c$  -- heat capacity per unit of mass;

$\rho$  -- density;

$c_p$  -- volume heat capacity.

Coefficients D and  $\alpha$  in gases with approximately equal molecular weights are near to each other.



Zel'dovich and Frank-Kamenetskiy showed that speed of flame is equal (in order of magnitude) to average diffusion rate of molecule on a section of its path before entry into reaction.

Further the problem is solved by the authors exactly with all dimensionless factors; there is derived the formula of speed of propagation of flame; there is solved the problem, to what conditions it is necessary to attribute the time of reaction in the flame.

Temperature of self-ignition under usual conditions corresponds to period of induction, from several seconds to several tenths of a second. In the flame propagating with speed 1 m/sec, with width of zone of flame on the order of 0,1 mm, entire interval from initial temperature to temperature of combustion is passed through in  $10^{-3}$  sec.

If into the formula describing speed of propagation of flame, taking into account temperature of ignition,

$$u_s = \sqrt{\frac{\tau(T_r - T_s)}{\tau(T_s - T_0)}}, \quad (2.2)$$

where  $T_B$  -- temperature of ignition;

$T_r$  -- temperature of burning,

is substituted expression characterizing dependence of period of induction on temperature of ignition,

$$\tau = e^{E/RT_0}, \quad (2.3)$$

where  $E$  -- activation energy,

there can be obtained expression for speed of propagation of flame as function of temperature of ignition. In this case maximum speed of propagation of flame is obtained with selection of temperature of ignition very near to temperature of combustion:

$$T_0 = T_r - RT_r^2/E. \quad (2.4)$$

It follows from this that within the limits of the theory, using temperature of ignition, it is necessary that temperature of ignition approaches temperature of combustion. Thus, for propagation of flame, kinetics of chemical reaction at temperature near to combustion temperature appears essential.

Chemical reaction in flame proceeds under complicated conditions. Heating of fresh fuel gas mixture is accompanied by penetration into it of products of combustion depletion of fuel in the mixture. Zel'dovich and Frank-Kamenetskiy showed that in fuel mixture for which  $x \approx D$ , connection between temperature and composition of mixture in flame coincides with connection between temperature and composition at adiabatic carrying out of chemical reaction. Such a connection is obtained with simple (without loss of heat) mixing of fresh mixture, taken at initial temperature, with products of total combustion, taken at theoretical combustion temperature. It turns out that in any zone of front of flame relative increase of temperature and relative changes of concentrations of all reacting substances are identically equal to each other:

$$\frac{T-T_0}{T_1-T_0} = \frac{a-a_0}{a_1-a_0} = \frac{b-b_0}{b_1-b_0} \quad (2.5)$$

where  $T_0, a_0, b_0$  — temperature and concentrations of substances A and B of original mixture;

$T_1, a_1, b_1$  — temperature and concentrations in final reaction products;

$T, a, b$  — temperature and concentrations in arbitrary place of the zone of flame.

In Fig. 7 is presented diagram of change of temperature and concentration of reacting fuel mixture in the front of the flame.

Formula (2.5) expresses similarity of fields of concentrations to field of temperature in flame, which means that temperature and concentration are connected among themselves just as during adiabatic flow of reaction in a closed volume, although in the flame, adiabatic conditions do not exist.

In flame and during adiabatic reaction (adiabatic explosion) connection between

temperature and concentration is one and the same; the substance passes through the same series of states. Completely different, however, is the kinetics of development of the process in time. Rise of temperature in adiabatic explosion due to self-heating of mixture during course of chemical reaction is replaced in flame by much faster heating — by thermal conduction. On the other hand, heat dissipation slows down in flame the last stage of completion of the reaction. Exponential growth of chemical reaction rate with temperature leads to the fact that in the flame, where there is realized a whole successive interval of temperatures from  $T_0$  to  $T_r$ , chemical reaction proceeds mainly near combustion temperature. Due to this there is present the possibility, in a comparatively simple theory, to determine the magnitude of normal speed of flame.

For approximate integration of heat-conduction equation Zel'dovich and Frank-Kamenetskiy consider that quantity of heat expended on increase of temperature of reacting substance to combustion temperature in the zone, in which reaction actually proceeds is small compared to total heat of reaction. Approximately, it is possible to consider that all heat from zone of reaction is dissipated by thermal conduction to unreacted gas.

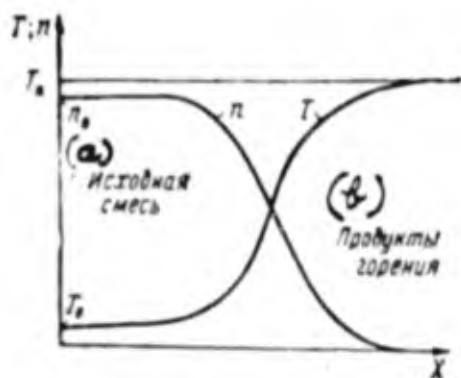


Fig. 7. Diagram of change of temperature and concentration of reacting fuel mixture in the front of the flame ( $n = a, b$ ;  $n_0 = a_0, b_0$ ).  
KEY: (a) Original mixture;  
(b) Combustion products.

For actual zone of reaction, disregarding expenditure of heat on heating of mixture and considering in this zone thermal conduction to be constant and equal, for determination of thermal capacity  $\lambda$  of products of reaction at  $T_r$  authors obtain following heat-conduction equation for one-dimensional propagation of flame along coordinate  $X$ ;

$$\lambda \frac{dT}{dx} = \Phi(T). \quad (2.6)$$

where  $\Phi(T)$  -- volume rate of heat release in zone of flame having temperature  $T_r$ .

Integrating (2.6) in quadratures and considering boundary condition

$$\frac{dT}{dx} = 0 \text{ at } T = T_r, \quad (2.7)$$

$$\frac{dT}{dx} = \sqrt{\frac{2}{\lambda} \int_{T_r}^T \Phi(T) dT}.$$

In order to find  $dT/dx$  on boundary of zone of reaction, we must place in (2.7) as the lower limit of the integral, the temperature on boundary of zone of reaction.

Since  $\Phi(T)$  rapidly decreases with drop <sup>of</sup> temperature (rate constant by law of Arrhenius decreases in interval of temperature  $RT/E$  by  $e$  times), authors find limiting value of  $(dT/dx)_z$  on boundary of zone of reaction differing from true value by the formula

$$\left(\frac{dT}{dx}\right)_z = \sqrt{\frac{2}{\lambda} \int_{T_r}^T \Phi(T) dT}. \quad (2.8)$$

At last, equating thermal flux from zone of reaction to total quantity of heat released in flame per unit of time, Zel'dovich and Frank-Kamenetskiy obtain

$$\lambda \left(\frac{dT}{dx}\right)_z = u_p Q, \quad (2.9)$$

where  $u_p$  -- mass rate of combustion (in grams of mixture per unit of time on  $1 \text{ cm}^2$  of surface of flame);

$Q$  -- caloric value of mixture (in calories per gram).

From comparison of formulas (2.8) and (2.9) there is obtained final expression for mass rate:

$$u_m = u_p \rho = \frac{1}{Q} \sqrt{2\lambda \int_{T_r}^T \Phi(T) dT}. \quad (2.10)$$

In expression (2.10) it is necessary to remember that

$$\Phi(T) = \Phi(T_r, T_0, T, a_0, a, \dots). \quad (2.11)$$

due to equation (2.5) final temperature

$$T_f = T_0 + \frac{Q}{c}, \quad (2.12)$$

where  $c$  — heat capacity of reaction products, depends on initial temperature and caloric value of combustible gas mixture.

In conclusion one should note that in majority of cases, chemical reactions in flames proceed by chain mechanism. This statement does not at all deny the paramount role of thermal conduction in propagation of flame, since probability of branching of chains, number of active centers, and this means also rate of chain reaction, — all these parameters of chain flow of reaction to a great degree depend on temperature.

At room temperature concentration of active centers and rate of chain reaction remain insignificantly small.

## Section 2. Dependence of Normal Speed of Flame Upon Parameters of Combustible Mixture

### 1. Dependence of Normal Speed of Flame on Pressure

Study of influence of pressure on normal speed of propagation of flame has great value. By it, it is possible to judge concerning character of actual process of propagation of flame.

Nagel [19] investigated influence of pressure on speed of propagation of flame in closed cylinders from 1 to 60 atm (tech). Inasmuch as combustion in closed cylinders is associated with increase of pressure and temperature, and also with motion of the actual burning gas, investigations of such type do not give any idea concerning influence of pressure on normal speed of propagation.

Experiments in study of influence of pressure on  $u_n$  with oxygen mixtures of carbon, monoxide butane, etc., were carried out by Stevens by a method developed by him (method of bomb of constant pressure) at pressures 200, 760, 2030 mm Hg. Results of experiments of Stevens indicate independence of linear speed of propagation of flame on pressure.

Flock and King [20] in detail investigated (in bomb of constant volume) influence of concentration of water vapor and pressure on rate of combustion of stoichiometric mixture of carbon monoxide with oxygen. From these data it is clear that at constant partial pressure of water vapor, combustion rate falls with increase of pressure.

Khitrin [21], working with mixtures of benzene and ethyl ether with air at pressures from 1 to 3.5 technical atmospheres by method of Stevens, established that linear speed of propagation of flame diminishes with increase of pressure, but mass rate of combustion grows.

Dependence of speed of propagation of flame on pressure is connected with dependence of rate of chemical reaction on pressure, i. e., with order of reaction in flame. Above, it was established that

$$u_n = \frac{\sqrt{\lambda \int_{T_0}^{T_f} \Phi(T) dt}}{\rho Q}, \quad (2.13)$$

where  $\lambda$  -- thermal conductivity;

$\rho$  -- density;

$Q$  -- caloric value of mixture;

$\Phi(T)$  -- rate of release of heat, proportional to rate of reaction in flame and depending on temperature.

Inasmuch as density is proportional to pressure, rate of reaction depends on pressure according to law  $p^n$  ( $n$  -- order of reaction), and thermal conductivity and reaction energy of reaction do not depend on pressure, we can write

$$u_n \sim p^{\frac{n}{2}-1}, \quad (2.14)$$

where  $p$  -- pressure;

$n$  -- order of reaction in flame.

This connection between order of reaction and dependence of speed of flame on pressure was established by Zel'dovich and Frank-Kamenetskiy.



## 2. Dependence of Normal Speed of Propagation of Flame on Temperature

Normal speed of flame noticeably grows with increase of initial temperature of mixture. According to theory of Zel'dovich and Frank-Kamenetskiy [13], mass rate of combustion depends on initial temperature through the temperature of burning, which is connected with initial temperature by equations of thermal balance. Increase of initial temperature of mixture leads to increase of temperature of zone of reaction, and this means, also to increase rate of the latter.

Dependence of speed of flame on temperature of combustion, as follows from theory of normal speed, is expressed by equation

$$u_n \sim e^{-E/2RT}, \quad (2.15)$$

where E -- heat of activation of reaction.

Passauer [22] studied influence of preliminary heating of mixture on normal speed of propagation of flame for mixtures with air of hydrogen, carbon monoxide, ethylene, acetylene, methane and other combustible gases.

On the basis of results of his investigations Passauer derived empirical dependence of linear speed of propagation of flame on absolute temperature:

$$u_n \sim T_0^2. \quad (2.16)$$

Consequently, mass rate is proportional to absolute temperature:

$$u_p \sim T_0^3. \quad (2.17)$$

Passauer considers that speed of flame becomes zero at absolute zero, "where thermal motion is stopped". However, Zel'dovich, based on the fact that during combustion of mixture cooled to absolute zero, temperature of combustion at a given composition remains high, considers the assumption of Passauer concerning tendency of  $u \rightarrow 0$  as  $T \rightarrow 0$  groundless [181].

In Fig. 8 and 9 are presented results of experiments of Passauer for mixtures of hydrogen and city illumination gas with air, and in Fig. 10 -- results of measurements of Tamman and Thile [23] of speed of flame, performed with the help of Bunsen burner for mixture of carbon monoxide with air.



Voronkov and Sokolik [24] investigated influence of temperature on speed of uniform propagation of flame in a pipe. They succeeded in establishing increase

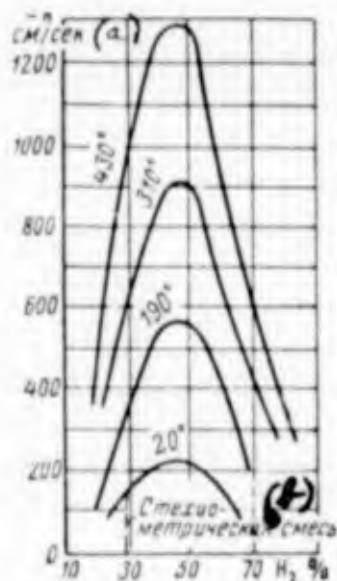


Fig. 8. Normal speeds of flame in hydrogen-air mixtures for different compositions and temperatures (Passauer).  
KEY: (a) cm/sec; (b) Stoichiometric mixture.

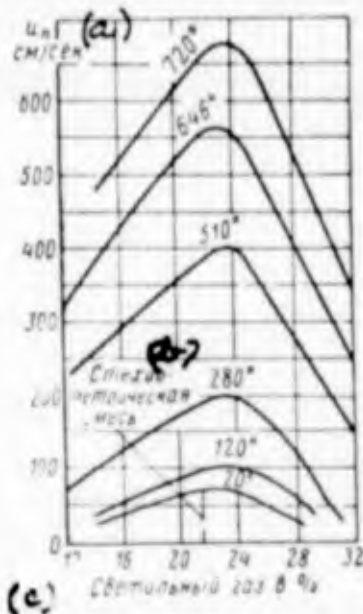


Fig. 9. Normal speeds of flame in mixtures of illumination gas with air at different compositions and temperatures. KEY: (a) cm/sec; (b) Stoichiometric mixture; (c) Illumination gas in %.

of speed of flame with temperature for mixtures, near in composition to upper and lower limits of propagation of flame. Old theories of normal speed of flame, using

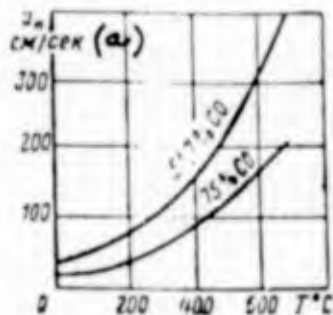


Fig. 10. Dependence of normal speed of flame in mixture of carbon monoxide with air on temperature.  
KEY: (a) cm/sec.

ideas concerning temperature of ignition  $T_B$  postulate  $u \rightarrow \infty$  at  $T \rightarrow T_B$ . Experiments of Voronkov and Sokolik refuted this assertion, since  $u$  remains finite near  $T_B$ .

### 3. Dependence of Normal Speed of Flame on Composition of Mixture

Dependence of normal speed of flame on air-fuel ratio is one of main points of departure for construction of theory of combustion. Long ago was established the strong catalytic influence of water vapor on burning of carbon monoxide. Small additions of water and hydrogen containing substances have an especially strong

influence of speed of propagation of flame.

Flock and King [20] investigated influence of water vapor on normal speed of propagation of flame in stoichiometric mixture ( $2CO + O_2$ ). Bunte with collaborators [25] established equivalence of action of water, hydrogen, methane, hexane and so forth upon mixture of them to dry mixture of carbon monoxide.

Processing of data of Ubbelode, Passauer, Bunte, Flock, Marvin and King, carried out by Zel'dovich and Barskiy, shows that at small concentrations of water vapor, there occurs the following relationship:  $u_n \sim \sqrt{[H_2O]}$ .

$$(2.18)$$

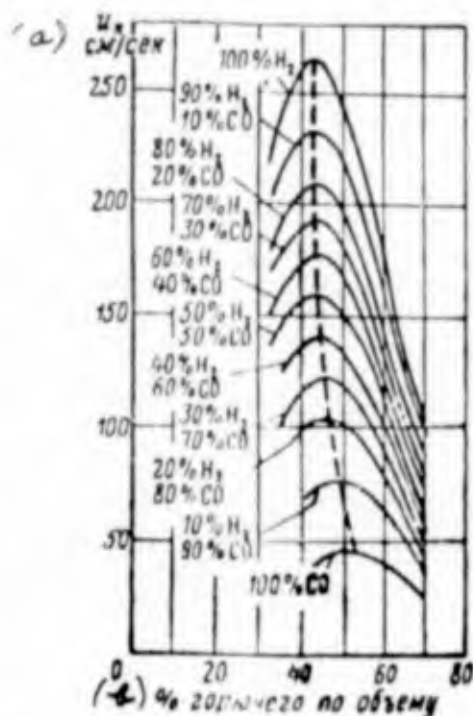


Fig. 11. Dependence of normal speed of mixture ( $CO + H_2$  air) on percent of fuel. KEY: (a) cm/sec; (b) % fuel according to volume.

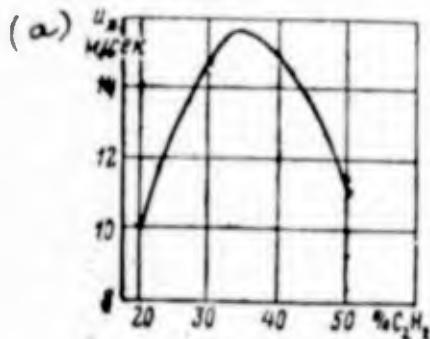


Fig. 12. Normal speeds of flame of acetylene-oxygen mixtures (Aliyev, Roslovskiy, Shaulov). KEY: (a) m/sec.

At large concentrations of water vapor, speed of flame increases more slowly. This circumstance is fully understood, since along with catalytic effect, water vapor acts as inert diluent, lowering the temperature of the zone of combustion.

Barskiy and Zel'dovich [26] in detail investigated this dependence and established that for mixture with surplus of carbon monoxide, rate of reaction in flame

is proportional to content of water or hydrogen, but for mixtures with surplus of oxygen -- to square root of their concentration.

Change of concentration by addition of inert impurities also will lead to change of temperature of combustion and, consequently, speed of propagation of flame. Experimentally there was investigated dependence of speed of flame on concentration of fuel for mixtures with oxygen and air. In Fig. 11 and 12 is represented the dependence of normal speed of flame for air ( $\text{CO} + \text{H}_2$ ) and oxygen mixtures on percent of fuel component. Thus change of composition is accompanied by change of temperature of combustion.

#### 4. Action of Various Impurities on Speed of Flame

Dixon [27] for the first time discovered the nonexplosiveness of dry mixtures of carbon monoxide with oxygen. Baker showed that completely dry detonating powder at the temperature of red incandescence does not explode, while a non-dry mixture reacts violently with explosion. Dixon, by his classical investigations proved that explosiveness of mixtures of carbon monoxide with oxygen was caused by the presence of water vapor or gas containing hydrogen. Speed of propagation of flame grows with increase of degree of humidity up to a content of 5.6% water vapor, but upon further increase of percentage content of moisture, it acts as an inert diluent. With addition of small quantities of moisture, speed of flame noticeably changes, but temperature of combustion remains practically constant. Dependence of speed of flame on concentration of moisture should be attributed to increase of chemical reaction rate.

Zel'dovich and Semenov, studying dependence of speed of flame on concentration of water vapor, proposed the following formula:

$$u \approx \sqrt{n_{\text{H}_2\text{O}}}$$

where  $n$  -- concentration of water vapor.

Barskiy and Zel'dovich [26] experimentally showed that in mixtures with surplus of oxygen, speed of flame is proportional to square root of concentration of water

vapor.

$$u \approx \sqrt{\pi_{H_2O}}$$

but in mixtures with shortage of oxygen

$$u \approx \sqrt[4]{\pi_{H_2O}} \quad (2.19)$$

Substances which during their small addition, hamper or completely stop propagation of flame are known under name flegmatizers. These negative catalysts are halides, their derivatives and certain other impurities.

Drozdo and Zel'dovich [28], studying action of carbon tetrachloride on combustion of mixtures of carbon monoxide with oxygen, established that speed of flame for mixture ( $200 + O_2 + 2\% H_2O$ ) equals 90 cm/sec; addition of 1.8%  $CCl_4$  decreases speed of flame to 40 cm/sec, and addition of 4.5%  $CCl_4$  decreases speed of flame by 16 times. With further increase of concentration of carbon tetrachloride (above 5%) propagation of flame becomes impossible.

Joresen and collaborators in detail studied propagation of flame of triple and four fold fuel mixtures with different contents of impurities. They established that the very best flegmatizers and Halogens and their compounds ( $CCl_4$ ,  $SnCl_4$  and so forth).

Kokochashvili [29] showed that the presence of HCl noticeably lowers speed of flame. Zel'dovich notices that action of HCl can result in transformation of atomic hydrogen into less active molecular form



and in mixtures where water vapor and hydrogen are absent, without HCl the mixture does not burn and HCl plays the role of a supplier of hydrogen. There are known also other cases of phlegmatization. Addition of excess quantity of fuel to stoichiometric mixture of methane with air renders 5 times more flegmatizing action than addition of an inert diluent of nitrogen.

Zel'dovich [30] explains action of methane by high-temperature endothermic

chemical reactions with products of combustion of methane ( $\text{CH}_4 + \text{CO}_2 = 2\text{CO} + 2\text{H}_2$  --- 56 kilocalories), as a result of which, temperature of combustion is lowered more strongly than with dilution by inert gas with the same heat capacity (nitrogen).

Nasirov and Shaulov [31], investigating kinetics of combustion of mixtures of nitrogen peroxide with hydrogen, established that with dilution of combustible mixture by nitric oxide, with increase of percent of NO in mixture speed of flame is decreased by more than with dilution by the inert diluent nitrogen. Addition to fuel mixture of 25% NO decreases speed of flame by approximately 3 times. Sharp lowering of speed of flame is observed for investigated mixtures with surplus of oxidizer ( $\alpha = 1.0$  to  $2.5$ ). This very interesting effect of self-inhibition in the front of the flame is explained by the authors by the fact that in view of the unpaired electronic structure, nitric oxide possesses high level of activity relative to free radicals. This property of nitric oxide also determines inhibition of chain reactions at average temperatures.

Interesting is the influence of impurities of acetylene on speed of propagation of flame in detonating mixture. At content of impurity of acetylene of 10%, in the mixture speed of flame is a maximum and exceeds the speed of flame in detonating mixture by two times. Content in mixture of 1%  $\text{C}_2\text{H}_2$  decreases speed of flame in detonating mixture by 50%. Such decrease of speed of flame, in all probability, can be provided only by destruction of large number of active centers (H-atoms) in flame.

### Section 3. Theory of Limits of Propagation of Flame

Earlier we considered propagation of flame under different conditions of experiment from the point of view of the connection of speed of propagation of flame with kinetics of chemical reaction. Now we will discuss question about limits of propagation of flame, important for entire theory of combustion, and those conditions under which propagation of flame becomes further impossible and flame dies out.



It is necessary to develop principally correct views of the question of limit of propagation of flame. Until now, in works of German scientists (Bunte, Jahn) there have been met naive ideas concerning limits of propagation of flame. From the point of view of these authors, limits of propagation of flame will be attained when temperature of combustion becomes equal to temperature of ignition. If temperature of combustion is lighter than temperature of ignition, propagation of flame is possible. With lowering of temperature of burning below the indicated limit due to heat losses or lowering of calorific value of mixture, propagation of flame becomes impossible. For limiting conditions, formulas of the theory of propagation of flame which uses the concept of temperature of ignition, identically give speed of flame equal to zero.

Jahn [32] considers speed of propagation at the limit equal to zero and uses this for extrapolation of speeds of propagation measured far from the limits, as well as finding of magnitude of temperature of ignition. With such views it is impossible to agree. Above we indicated shortcomings of theory of propagation of flame using concept of temperature of ignition.

Calculation of limits of propagation of flame according to Jahn leads to values of temperature of ignition lying above temperatures of self-ignition measured under usual conditions. This confirms arbitrary character of the quantity, temperature of ignition in the theory. During strict carrying out of calculations and consideration of heat transfer to walls, Daniell, also using concept of temperature of ignition, obtained other conclusions concerning limits of propagation of flame.

From the physical point of view, the lower the speed of propagation of flame, the greater the role of heat transfer and the greater the drop in temperature as compared to the theoretical temperature of combustion. Therefore, under the conditions when fast flame can still be propagated in mixture of given composition with given caloric value, slowly propagating flame will develop a temperature which is too low (lower than the temperature of ignition) and its propagation will

be stopped. Daniell, developing these considerations, decided that in the presence of heat transfer, speed of propagation of flame at the limit should be different from zero.

Developing further theory of propagation of flame, Zel'dovich [33] considered question about limit of propagation of flame in a pipe. As we have seen, according to theory of Zel'dovich, speed of propagation of flame depends on temperature of combustion, according to the law

$$u = e^{E/RT} \quad (2.20)$$

where E -- activation energy, inasmuch as chemical reaction rate in flame equals

$$u = \text{const} e^{-E/RT} \quad (2.21)$$

On the other hand, in the presence of heat transfer, temperature of combustion itself depends on speed of flame. The greater the chemical reaction rate, the nearer should be temperature of combustion attained in flame to theoretical temperature of combustion calculated on the assumption of adiabatic flow of chemical reaction.

Losses of heat of reaction in not very wide pipes are determined by heat transfer from heated reaction products to walls of pipe, and from the latter -- into surrounding space. Heat loss of a unit of volume of gas per unit of time equals

$$\pi = \beta \frac{f}{V} (T_f - T_0) \quad (2.22)$$

where  $f/V$  -- ratio of surface of flame to volume;

$\beta$  -- coefficient of heat transfer, characterizing thermal losses.

During burning in pipes of smaller diameter, heat transfer is increased. There exists so-called critical diameter of pipe, with which propagation of flame becomes impossible. Mechanism of loss of heat consists in transfer of heat out of zone of combustion, partially cooling reaction products.

As Zel'dovich showed [2], if not all heat of reaction goes to heat the mixture, than temperature of combustion

$$T_c = T_{\text{Theor}} - \frac{\beta}{\dots} \quad (2.23)$$



Quantity of heat lost during combustion is inversely proportional to rate of reaction, i. e., proportional to time of chemical transformation.

Basis of theory of propagation of flames, which includes question about limit of propagation of flame, is joint consideration of two equations:

1) equation of dependence of speed of flame on temperature of combustion, ensuing from theory of propagation of flame;

2) equation of dependence of temperature of combustion on speed of flame, ensuing from consideration of thermal losses during propagation of flame.

Obtained relationships are most simply illustrated graphically. In Fig. 13 as an example are constructed graphs for a mixture whose speed of propagation of flame  $u = 104a \frac{40,000}{2 RT_r}$ . Theoretical temperature of combustion (curve 1) for this mixture

$$T_{Theor} = 2000^\circ K.$$

Let us consider combustion of mixture under the conditions of heat transfer, characterized by two values of coefficient  $\beta$  ( $5 \cdot 10^5$  and  $1,5 \cdot 10^5$ ). According to these values of  $\beta$  we will obtain in Fig. 13 with two broken curves 2 and 3, calculated by formula (2.23). With small heat transfer ( $\beta = 1,5 \cdot 10^5$ ) we have two solutions: curves 1 and 3 intersect at two points. Point A corresponds to stable regime, with which temperature differs little from temperature of combustions. During large heat transfers curves 1 and 2 do not intersect. Equations of propagation of flame and heat transfer do not have a joint solution; therefore, propagation of flame is impossible.

Limit of propagation of flame (curve 4) corresponds to condition of tangency of curves, i. e., transition from regimes of type of location of curves 3--1 to type of curves 2--1. It is possible to show that at limit of propagation of flame (approximately)

$$T_r = T_{Theor} \frac{RT_{Theor}}{E}$$

In our case at the limit

$$T_r = 2000 - \frac{2(2000)^2}{4000^2} = 1800^\circ \text{K}.$$

Speed of flame at limit is 10 times less than the value  $u_{\text{Theor}}$ , which it would have if there were no heat losses. So, in our example  $u_{\text{Theor}} = 10^4 e^{-\frac{2000}{2000}} = 65 \text{ cm/sec}$ . At the limit of propagation, speed of flame falls to  $65 \cdot 10^{-1} = 6.5 \text{ cm/sec}$ . Accordingly  $u_{\text{lim}} = 10^4 e^{-\frac{2000}{1800}} \cdot 10^{-1} = 39 \text{ cm/sec}$ .

Limiting value of coefficient  $\beta$  characterizing heat transfer, we find from condition

$$1800 = 2000 - \frac{\beta}{39^2},$$

whence  $\beta = 3.2 \cdot 10^5$ .

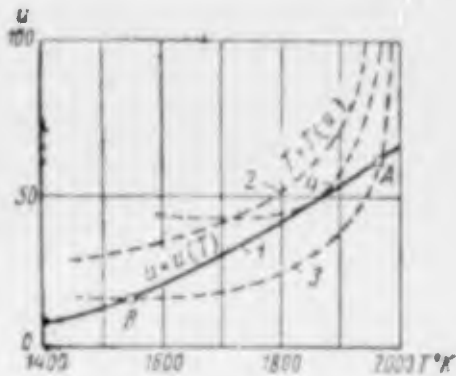


Fig. 13. Graph of determination of critical conditions of propagation of flame in pipes (Shaulov).

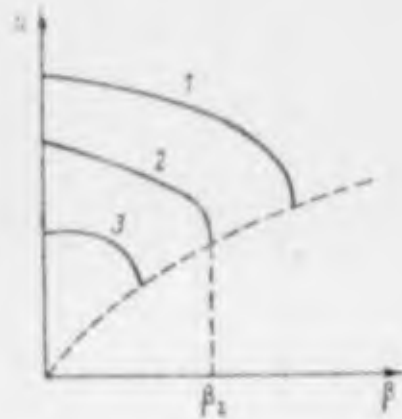


Fig. 14. Lowering of speed of flame in pipe with increase of heat losses and appearance of critical phenomena (Shaulov).  
1, 2 and 3 -- at different constant values of  $\beta$ .

Propagation of flame with speed less than 39 cm/sec is impossible. Thus, the assertion of Jahn concerning equality to zero of speed of flame at limit of propagation appears to be erroneous.

Numerous experiments with the most varied combustible mixtures showed that at the limit, the speed of normal propagation is on the order of 5--7 cm/sec. According to theory of Zel'dovich, limiting speed of flame is lower, the less the heat transfer, inasmuch as at the limit

$$\frac{\beta}{u^2} = \frac{RT^2}{E}. \quad (2.24)$$

Dependence of speed of flame on coefficient  $\beta$  for mixtures of different composition, with various temperatures of combustion, and accordingly various theoretical speeds of flame (at  $\beta = 0$ ) is shown in Fig. 14.

For a given mixture, speed of flame is decreased with increase of quantity  $\beta$ . However, this decrease is limited by the fact that at a certain value of  $\beta$  (for example,  $\beta_2$  for curve 2 in Fig. 14), there will be attained the limit and propagation of flame is stopped. Comparing limiting value of speed for different values of  $\beta$  corresponding to different compositions of mixture, we obtain the dotted line of the dependence of maximum speed of flame on  $\beta$ . Limiting speed of flame is greater, the greater the heat transfer.

During propagation of flame in narrow pipes and fillings, heat transfer is determined basically by heat dissipation into the walls of the pipes or into the material of the packing. As we will see further, from this it does not at all follow that for the process thermal conductivity of packing and walls of pipe is important. On the contrary, main thermal resistance is the thermal resistance of the burning gas itself.

With decrease of linear dimensions of system: of the diameter of the pipe, dimensions of particles of the packing or the average dimension of pores, which are proportional to it, heat transfer to the walls rapidly increases. This occurs for two reasons: in the first place there is increased the ratio of surface to volume; secondly, heat transfer per unit of surface also is increased, since in the small-size system all temperature gradients are greater than in the large-size system.

Ratio of thermal flux to product of the size of the surface and the difference of temperatures, with geometrically similar fields of temperature, in small-size systems appears to be greater than in large-size systems. This simple consideration does not replace, obviously, the strict proof, from which was obtained

$$\beta = \frac{T_r - T_{Wall,2}}{d^2} \quad (2.25)$$

where  $d$  -- characteristic dimension of system (diameter of pipe, diameter of grains of filling or average diameter of pore);

$\kappa$  -- thermal diffusivity.

Depending upon determination of  $d$  numerical coefficient in front of the expression in the right number of (2.25) changes, it can be determined only by exact calculation. General form of formula (2.25) remains the same.

Rate of heat transfer from given volume of heated gas is proportional to first power of thermal diffusivity  $\kappa$ . However, during propagation of flame, the bigger the magnitude of  $\kappa$ , the bigger the volume out of which occurs heat transfer, the volume of the heated layer in the front of the flame and the volume of that region behind the flame, heat transfer from which lowers the temperature of the flame. Therefore, coefficient of heat transfer is proportional to the square of thermal of diffusivity  $\beta \sim \kappa^2$ .

Comparing (2.25) and (2.24), we obtain

$$\frac{(T_r - T_{\text{Wall}})^2}{u^2 d^2} = \frac{RT^2}{E}$$

or

$$\frac{ud}{\kappa} = \sqrt{\frac{E(T_r - T_{\text{Wall}})}{RT^2}} \quad (2.26)$$

All formulas considered here are correct with accuracy up to the numerical factors.

Limit of propagation of flame corresponds to a definite value of criterion of Peclet  $Pe = ud / \kappa$  known in theory of heat transfer, which is determined by speed of flame, characteristic dimensions of system and thermal diffusivity  $\kappa$ .

The wider the pipe, the lower the speed of the flame at the limit. One should note, however that with diameters of several centimeters, heat transfer by radiation becomes important. Its magnitude depends weakly on diameter. Thus the coefficient  $\beta$  ceases to depend on diameter, as this was observed in narrow pipes, according to (2.25). In pipes of large diameters, quantity  $\beta$  will attain a certain limiting

value, determined by radiation. Limits of propagation are not widened any more.

In narrow pipes, heat transfer is determined by thermal conduction. In air mixtures of different fuels at constant pressure, thermal diffusivity  $\alpha$  little depends on composition. For all of them at the limit  $d < 3-4$  cm.

$$ud = \text{const} \quad (2.27)$$

#### Section 4. Stability of Normal Front of Flame

In jet and rocket motors, process of combustion is always realized under the conditions of turbulent flow. Absence of a developed theory and clear concepts concerning turbulence in burning flow hampers formulation of problem about stability of such a form of combustion. Therefore, instead of investigation of turbulent flames, in which perturbation of flow has a very complicated nature, there is presented an analysis of influence of periodic or continuous disturbances on stationary front of flame in laminar flow.

Although such investigations are still insufficient for description of turbulent burning, they still have significant interest in the consideration of stability of operating process in motors. Problem of stability or instability of burning in the case of propagation of flame in a motionless gas mixture or in laminar flow was considered by Landau [34]. His solution, and also conclusions thus obtained, have value not only for theory of burning but also are examples of solution of the problem concerning stability, applied to a whole series of systems.

If width of zone of combustion is small compared to characteristic dimensions of vessel where chemical reaction occurs, the purely gas-dynamic problem becomes separable from the chemical problem. Therefore, disregarding thickness of zone of combustion, it is possible to consider stability of the interface between products of combustion and the fresh mixture. On this surface, state of gas experiences a jump, i. e., it represents a surface of discontinuity.

On surface of discontinuity should these be fulfilled conditions of continuity of mass flow, momentum and energy. As was shown by Landau and Lifshits [35], in the presence of a discontinuity of normal velocity, tangential component of velocity

of flow should be continuous, which leads to continuity of pressure and enthalpy.

Landau, disregarding viscosity, curvature of front and compressibility, by the method of small perturbations investigated boundary of stability of a plane front. The scheme of investigation of stability was the following: on undisturbed flow is superimposed a small perturbation, which is chosen so that the resulting disturbance satisfies equations of motion, continuity and boundary conditions.

Disregarding terms of second order of smallness, it is possible to consider linearized differential equations and solve the problem of stability by means of investigation signs of roots of characteristic equation of the system. In such a formulation, solution of problem takes the following form:

Let us consider element of surface of front of flame in system of coordinates XOY. Axis x is directed along the normal to this surface, and axis y along the tangential to it. Parameters of state of fresh gas will be designated by subscript "1", and parameters of combustion products — by subscript "2".

On the principle undisturbed motion of the flow will be placed a small perturbation  $p' = v' \sim \exp[i(ky - \omega t)]$ . We will substitute into the equations of Euler for plane motion:

$$\left. \begin{aligned} \frac{\partial u}{\partial t} + u \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} &= -\frac{1}{\rho} \frac{\partial p}{\partial x}, \\ \frac{\partial v}{\partial t} + u \frac{\partial v}{\partial x} + v \frac{\partial v}{\partial y} &= -\frac{1}{\rho} \frac{\partial p}{\partial y} \end{aligned} \right\} \quad (2.28)$$

and the equation of continuity.

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0. \quad (2.29)$$

Disregarding terms of the second order of smallness, we obtain

$$\left. \begin{aligned} \frac{\partial u'}{\partial t} + w \frac{\partial u'}{\partial x} &= -\frac{1}{\rho} \frac{\partial p'}{\partial x}, \\ \frac{\partial v'}{\partial t} + w \frac{\partial v'}{\partial y} &= -\frac{1}{\rho} \frac{\partial p'}{\partial y}, \\ \frac{\partial u'}{\partial x} + \frac{\partial v'}{\partial y} &= 0. \end{aligned} \right\} \quad (2.30)$$



Boundary conditions on surface of front of flame are determined from conditions of constancy of tangential component of velocity and equality of pressures along both sides of the front, and also from the fact that speed of propagation of flame is a constant quantity, not depending on perturbations.

Simultaneous solution of equations of perturbed motion, continuity and boundary conditions is written in the form of the following equality:

$$(-i\omega^2)(w_1 + w_2) + 2i\omega k w_1 w_2 + k^2 w_1 w_2 (w_1 - w_2) = 0. \quad (2.31)$$

As a result of analysis, Landau discovered that if flow velocity before the front of the flame is greater than velocity after the front ( $w_1 > w_2$ ) then front of flame is stable; if however,  $w_1 < w_2$  front of flame is unstable. Since density of products of combustion  $\rho_2$  is less than density of original products  $\rho_1$ , from conditions of continuity it follows that  $w_2 > w_1$ . Therefore Landau made conclusion concerning absolute instability of front of flame. Paradoxical conclusion of Landau became subject of large number of investigations. In opinion of authors, calculation of viscosity of fuel mixture, diameter of vessel, curvature and thickness of front of flame, obviously, should have effect on character of results of investigations of stability of front of flame. Structure of plane front of flame was studied by the method of schlieren photography by Markstein [36], and thus was detected a cellular structure. In a stable structure, cells of front are hemispherical, with individual dark ridges and are in rapid motion; in an unstable structure, cells are spherical and their motion is slowed down.

Upon transition to mixtures which are near to stoichiometric composition, cell structure disappears; front of flame is extended in a plain uniform disk.

Analyzing results of Landau, Markstein shows that with consideration of curvature of front of flame, it appears possible to coordinate experimental data with average dimensions of cell obtained from theoretical considerations.

Eibinder [37] explains appearance of cell structure of flame by change of mechanism of its propagation; front of flame is stable only during diffusion burning.



Theoretical investigations of stability of front of flame in viscous incompressible medium were carried out by Eibinder and Yagodkin [37], [38]. Results of these investigations are contradictory; therefore, question about influence of viscosity on stability of front of flame remains open.

Conclusion of Landau concerning absolute instability of plane front was also used by many investigators for explanation of mechanism of transition of normal burning into detonation, and the cause of appearance of turbulent burning. There were undertaken works to confirm this conclusion experimentally and discover the phenomenon of self-turbulence.

For the purpose of study of critical conditions for appearance of self-turbulence of normal burning, Shaulov [39] with a group of collaborators investigated self-turbulence by means of burning of mixtures of methane and <sup>acetylene</sup> with oxygen in a bomb of constant volume, as well as in large freely expanding transparent rubber spheres. Results of experiments in burning of the fastest burning hydrogen- and acetylene-oxygen mixtures [40] in a closed volume did not lead to observation of the effect of self-turbulence described by Zel'dovich and Rozlovskiy [41]. Considering that rigid walls of bomb prevent appearance of effect of self-turbulence, authors carried out further study by means of burning of large volumes of gas in freely expanding transparent rubber shell with subsequent photographic recording of propagating flame on revolving film.

There were not introduced fundamental explanations into the investigation of the nature of self-turbulence of normal burning by the interesting experiments of Markstein [36]. The effect of cellular structure of plane slow flames <sup>propagated</sup> in wide pipes discovered in these experiments is impossible to explain by self-turbulence normal burning by the mechanism proposed by Landau, and calculations of Markstein are inadequate for quantitative treatment of the phenomenon, since in them critical parameters of instability are too arbitrarily determined. Thus, the cause of stabilization of normal flame under usual conditions remain to this day unexplained.

Results of described experiments on appearance of spontaneous acceleration of spherical flame and transition to detonation conditions were reproduced after several years by Manson and Ferris [42]. These experiments were conducted in transparent rubber shells with volume of from 30 to 110 l.

Studying propagation of flame in methane-oxygen and acetylene-oxygen mixtures, Shaurov and Rozlovskiy [39] made an attempt to estimate lower limit of value of Reynolds number (if this criterion is decisive for such a phenomenon), corresponding to region of transition of normal burning to detonation. These experiments also were conducted in rubber transparent shells.

In all experiments with methane-oxygen mixtures, detonation was not observed; it was possible to realize it only during burning of acetylene-oxygen mixtures. Burning of the greater part of the investigated methane-oxygen mixtures was accompanied by acceleration of flame. Typical photographic recordings of these flames and one of their diagrams are shown in Fig. 15.

Change of density of gas mixture during combustion, value of which is necessary for calculation of normal speed of flame, in the first approximation can be estimated according to magnitudes of diameters of original sphere  $d_0$  and products of combustion  $d_r$ , namely:  $\mu = (d_r/d_0)$ .

Change of speed of flame in process of propagation is a measure of increase of its surface and turbulence of burning. Criterion of turbulence of front can be considered as the ratio of speeds of flame  $u_{n2}/u_{n1}$ , -- where  $u_{n1}$  -- true normal speed corresponding to initial section photographic recording and to the undisturbed front;  $u_{n2}$  -- conditional normal speed at final stage of burning.

Each of these quantities is determined by observed speed of flame  $u$  in relation to motionless combustion products  $u_n = u_r/\mu$ . By values of  $u_{n1}$  and  $u_{n2}$ , kinematic viscosity of original mixture and diameters of flaming spheres corresponding to the beginning of acceleration  $d_1$  and end of combustion  $d_r$ , it is possible to calculate corresponding values of Reynolds number  $Re_1$  and  $Re_2$ . Magnitude  $Re_1$  characterizes

lower limit of region in which there appear disturbances of front of flame,  $Re_2$  -- to the lower limit of region of appearance of spontaneous spherical detonation.

Interesting peculiarities are detected by photographic recording of combustion of mixtures (65%  $O_2$  + 35.0%  $CH_4$ ), near to stoichiometric composition (Fig. 16). At point A shown on the diagram and corresponding to  $d = 17,1$  cm (in this experiment  $d_0 = 23.3$  cm), there is observed a sharp increase of  $u_r = 44.5$  -- 152 m/sec. At  $d \approx 35$  cm, flame is slowed to  $u_{r2} = 91$  m/sec. In the second analogous experiment there also is observed an abrupt change of speed at  $d = 18.5$  cm to 164 m/sec, with subsequent slowing down.

Causes of attenuation of turbulence of flame after intermittent growth of speed are unclear, but the fact of such stabilization can not be doubted. It is probable that this phenomenon is combined with the entire problem of stability of normal burning, which is at variance with the hydrodynamic theory of self-turbulence.

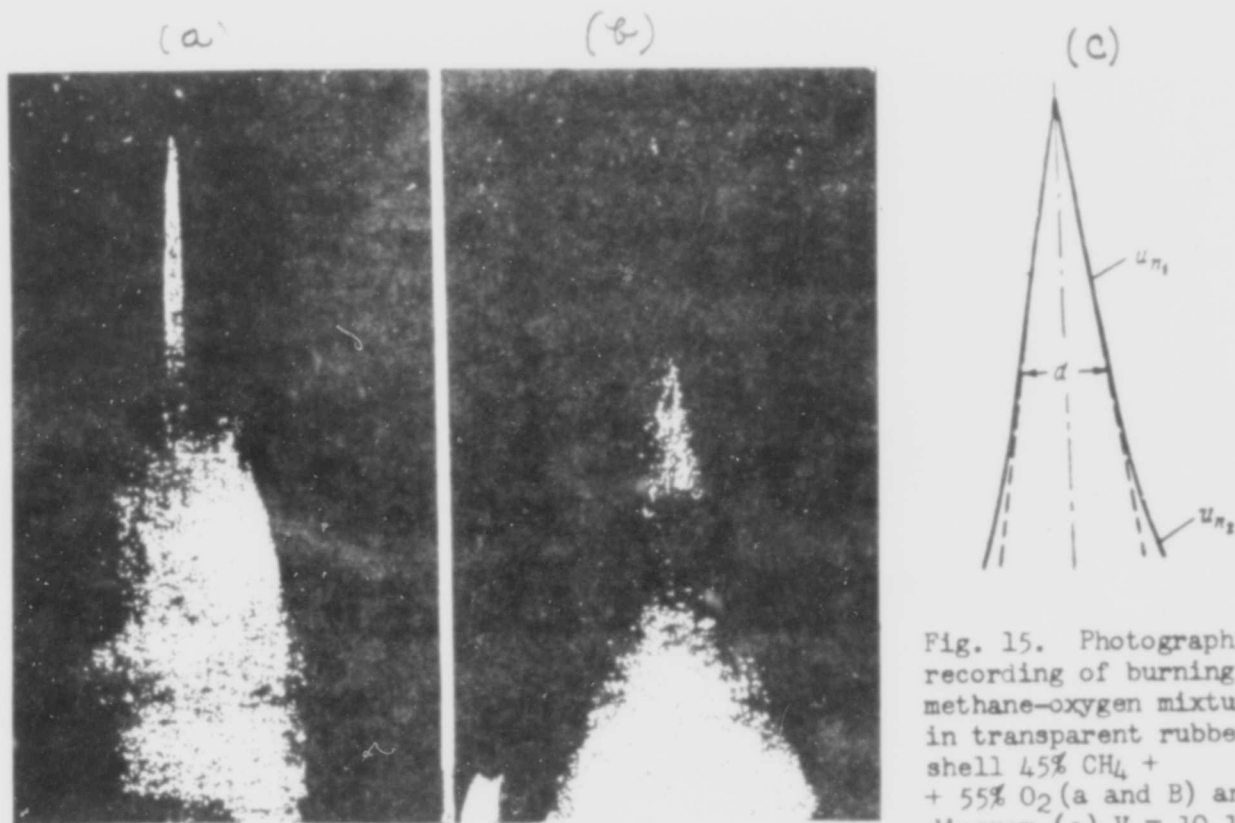


Fig. 15. Photographic recording of burning of methane-oxygen mixtures in transparent rubber shell 45%  $CH_4$  + 55%  $O_2$  (a and B) and diagram (c)  $V = 10 \frac{1}{2}$  (Shaulov et al. [39]).

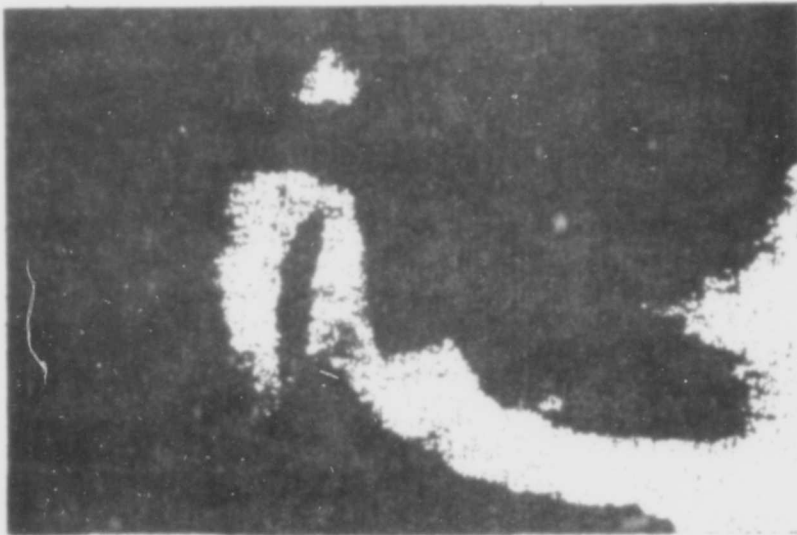


(a)



(b)

Fig. 16. Photographic recording of burning of methane-oxygen mixtures in transparent rubber shell (a) and its diagram (b). (35%  $\text{CH}_4$  + 65%  $\text{O}_2$ ,  $V = 6.7 \text{ l}$ ; see [47]).



(a)



(b)

Fig. 17. Photographic recording of burning of acetylene-oxygen mixture in transparent rubber shell (a) and its diagram (b). (50%  $\text{C}_2\text{H}_2$  + 50%  $\text{O}_2$ ;  $V = 5 \text{ l}$ ; see [47]).

In Fig. 17 are shown typical photographic recordings of burning of acetylene-oxygen mixtures (50%  $C_2H_2$ ;  $v = 5 \underline{1}$ ). Acceleration of flame starts at  $d_1 = 11$  cm;  $Re_1 = 1 \cdot 10^5$ . At  $d_2 = 23$  cm  $Re_2 = 3 \cdot 10^5$  at point D, corresponding to place of contact of front of flame with the detonation pipe, there appears a reflected shock wave, propagating through the combustion products with speed 2800 — 2900 m/sec, i. e., approximately equal to detonation speed for the investigated mixtures.

The track of propagation of shock wave on the photograph crosses line of propagation of front of flame from opposite direction, on which at this point is seen a break. Further propagation of flame in this direction occurs with speed on the order of 1100 — 1400 m/sec. Thus, spontaneous appearance of spherical detonation also in this case was not possible to be ascertained.

By generalizing works connected with investigations of stability of front of flame, we should indicate that there exists a bounded region of waves which leads to stability of the front of the flame. In connection with the fact that it is not possible to determine region of stability of plane front of flame, in practice, in consideration of process of combustion in technical apparatuses, front of flame is arbitrarily assumed to be stable.

If we consider the front of the flame as a surface, on which temperature, pressure and density change rapidly, then we thus obtain conditions placed by gas dynamics on surface of strong discontinuities. Disregarding tangential component of velocity, the process is described by equation of continuity of Euler and his equation of state for one-dimensional flow.

Stability of such a system was considered by Rauschenbakh [43]; he explained that, depending upon position of front along length of pipe, boundary of stability and spectrum of frequencies abruptly changes. Analogous results were obtained by Popov [44] in the consideration of stability of front of flame on boundary of separation between two columns of gas having different speeds of sound.

Popov showed that the nearer the front of the flame to closed end of pipe, the

higher the frequency, and at ratio of lengths 1 : 9, it constitutes approximately 500 cps.

Ban-Zelikovich [45], considering the cause of appearance of oscillations in pipes, established that process of their appearance can proceed in two different ways.

In one case normal burning evidently is disturbed (completeness of combustion sharply oscillates or sections of gas not yet touching front of flame spontaneously are ignited, and so forth). Thus abnormal burning is observed still before there appear more or less appreciable oscillations of gas. Besides, it is necessary to consider directly the course of the process of burning.

In another case visible disturbances in process of burning are not observed or are observed after appearance of perceptible pulsations of gas. However this does not mean that for appearance and development of oscillations the process of burning must be disturbed. Ban-Zelikovich, analyzing the second case, asserts that cause of appearance of oscillations in pipes in this case is the appearance of shock waves of weak intensity.

The presented brief information do not exhaust, certainly, the entire complexity of the problem. However, they are sufficient for account of existing attempts of explanation of mechanism of origination of instability of process of burning.

One of the causes of disturbance of stability of process of burning are conditions for flow of complicated chemical reactions. There exist a number of experimental facts which show that chemical reactions within a certain range of variables lead to establishment of a naturally oscillating process and can, obviously, serve as a model for explanation of the cause of appearance of instability of operating process in motors.

In works of Frank-Kamenetskiy, Sal'nikov et al. [46], [8] were proposed special kinetic schemes of flow of two consecutive reactions with different temperature dependence. These investigations showed that such a two-stage mechanism of reaction



leads to the case in which the process assumes a periodic character. There are distinguished basically oscillations of two forms: purely kinetic oscillations, and oscillations, connected simultaneously with kinetics of reaction, as well as with heat release and heat dissipation. Let us note that in all probability, thermo-kinetic oscillations depend on rates of release of heat per unit of volume, i. e., on heat release rate of chemical reaction.

In the example of disintegration of  $\text{NO}_2$ , let us consider the simplest form of thermokinetic oscillations, i. e. when in the reaction there participates one intermediate product X, according to the scheme



where  $v_1$  and  $v_2$  are rates of transformation.

In this scheme, transformation of NO into  $\text{N}_2$  occurs at higher temperature. Such two-stage burning with one intermediate reaction product NO was observed during burning of simplest nitroether  $\text{CH}_3\text{ONO}_2$  [47] and during burning of mixtures of hydrogen with nitrogen peroxide [48].

Full description of process of flow of chemical reactions is given by a system of two differential equations -- kinetic and thermal:

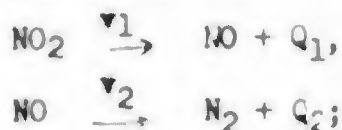
$$\frac{dx}{dt} = f - k(T)x, \quad (2.33)$$

$$\frac{dT}{dt} = \frac{q}{c_p} - \frac{as}{c_p u} (T - T_0), \quad (2.34)$$

$f$  -- rate of formation of intermediate product x (NO) from original substance A ( $\text{NO}_2$ );

$k(T)$  -- rate constant of transformation of x (NO) into final products B ( $\text{N}_2$ ), which depends on temperature more strongly than A;

$q$  -- rate of heat release, depending on rates of both reactions



$a$  — coefficient of heat transfer;

$T$  — temperature of reacting mixture;

$T_0$  — temperature of environment;

$Q_1, Q_2$  — reaction energies of reactions;

$c$  — heat capacity of reacting mixture;

$\rho$  — its density;

$\omega$  — volume of reacting system;

$s$  — external surface through which occurs heat transfer.

Since rate of second reaction ( $\text{NO} \xrightarrow{\nabla_2} \text{N}_2$ ) depends more on temperature than rate of first reaction ( $\text{NO}_2 \xrightarrow{\nabla_1} \text{NO}$ ), and heat release to a significant degree is connected with second reaction, process can assume naturally oscillating character. Accumulation of intermediate product A (NO) should lead to increased by heat release due to second reaction  $\text{NO} \rightarrow \text{N}_2$  and corresponding increase of temperature. Increase of temperature will increase rate of consumption of intermediate product NO more strongly than rate of formation; thus, concentration of NO diminishes, which will lead to lowering of temperature, etc.

This conclusion is confirmed by mathematical analysis. With specific assumptions concerning dependence of  $f, k, q$  on temperature and concentration, it is possible to show possibility of appearance of natural oscillations.

Solution of system of equations (2.33) and (2.34) was carried out by Sal'nikov and it was shown that under definite conditions these solutions can have an oscillatory and periodic character. Besides kinetic and thermokinetic oscillations, there are possible still relaxation oscillations, appearing in dependence on rate of supplying of fuel mixture into combustion chamber.

## Section 5. Turbulent and Detonation Combustion

### 1. Turbulent Combustion

Elements of theory of combustion, considered above embrace not nearly all phenomena observed during combustion of fuels in technical apparatuses. Operating

processes in motors have a much more complicated character than processes, which are described by theory. Thus, for example, normal burning with plane front and a definite speed, as Zel'dovich stresses, is the exception. We study it only under laboratory conditions, but phenomena proceeding in motors have quite a different character.

Processes of burning proceeding in technical apparatuses are complicated, first of all by the presence of turbulent motion of fuel mixture. Under action of turbulence in internal-combustion engine, air-breathing jet engine and liquid-fuel rocket engine, abruptly is increased speed of propagation of flame, due to which it becomes possible to significantly intensify the process of combustion.

Turbulence can increase transfer of heat along front of flame without rendering an influence on flow of chemical reactions. Such influence of turbulence on increase of speed of propagation of flame is possible during burning of uniform mixture. We meet with this type of turbulent combustion in practice only in internal-combustion engine with ignition from spark. In all remaining technical apparatuses, process of combustion occurs simultaneously with process of mixing of fuel and oxidizer, which are broken up in the form of separate volumes in the gas flow. Here, under action of turbulence, first of all are accelerated chemical reactions, and processes of heat transfer have only secondary importance. This form of combustion, whose rate is determined by process of mixing, and whose intensification becomes possible under action of turbulence, is considered in works [49]--[53].

It is obvious that such combustion, called by Frank-Kamenetskiy micro-diffusion turbulent combustion, is the most wide-spread case of burning, by means of which are described basically all operating processes of present day motors.

What is characteristic for burning in turbulent flow?

First of all, for appearance of turbulent combustion, as well as for any turbulent flow, it is necessary that forces of inertia be significantly larger than forces of viscosity. Reynolds number, characterizing ratio of these two forces,

should be greater than a certain critical value (near 2300).

In the region of developed turbulence, i. e., in the region which is far from the critical value of Reynolds number, forces of viscosity lose their importance and structure of turbulent flow is characterized by quantities which are analogous to those which are considered during processes in laminar flow. Thus, for example, molecular motion is characterized by mean free path and velocity of molecules; similar to this, turbulent motion is characterized mixing length and pulsation of velocity.

Mixing length  $l$  is the distance at which there still appears a connection between pulsations, or the distance through which a separate volume separated from turbulent flow can pass without changing its individuality. Velocity, with which occurs movement of these volumes, is called pulsation velocity. Velocity of flow in every moment of time can be represented in the form of the sum of mean value  $\bar{w}$  and deviation from it (pulsation of velocity). Root-mean-square value of pulsation velocity designated  $w'$ , is characteristic parameter of turbulent flow. Intensity of turbulence or simply turbulence is determined by ratio  $w'/\bar{w}$  (called sometimes Karman's number).

A characteristic of turbulent flow is also the scale of turbulence, i. e., linear dimension of elementary volume.

During combustion in turbulent flow, an important property of it is intensity of mixing of separate volumes of gas.

Intensity of turbulent mixing is determined by coefficient of turbulent exchange  $A$ , having the meaning of coefficient of kinematic viscosity in the case of momentum transfer, thermal diffusivity in the case of heat transfer and diffusion coefficient during transfer of mass:

$$A \sim \nu, \quad -a, D, \sim lw'. \quad (2.35)$$

Turbulent coefficients of viscosity, thermal diffusivity and diffusion are hundreds and thousands of times greater than the corresponding coefficients of molecular transfer.

Besides these characteristics, turbulent combustion, as in the case of propagation of flame in a motionless gas mixture and in laminar flow, is characterized also by the speed of burning. Speed of turbulent burning is not a physicochemical constant of the fuel mixture, but depends on intensity and scale of turbulence. During small-scale turbulence, i. e., when mixing length is insignificant and small compared to thickness of front of flame, speed of burning depends not only on kinetic, but also on diffusion factors [28]. This case hardly has practical value. During large-scale turbulence front of flame is broken up, so that separate volumes of mixture burn. Speed of burning thus is determined only by diffusion factors.

Below we will consider results of works which serve as a basis on which are constructed all investigations into turbulent combustion.

In the most simple way, consideration of influence of turbulence on speed of burning in uniform mixture is possible, if we consider turbulent flow as flow in which thermal diffusivity  $\frac{a}{\tau}$  is significantly greater than molecular thermal diffusivity  $a$ . According to this, the formula for speed of turbulent burning takes the form

$$u_t \sim \sqrt{\frac{a_r}{\tau}} \sim \sqrt{\frac{l w'}{\tau}}$$

or more accurately

$$u_t \approx \sqrt{\frac{a + a_r}{\tau}} \sim \sqrt{\frac{a + l w'}{\tau}} \sim \sqrt{\frac{a}{\tau} \left(1 + \frac{l w'}{a}\right)}. \quad (2.36)$$

If time of flow of chemical reaction under influence of turbulence remains constant, then it can be determined directly through normal speed of propagation of flame:

$$\tau \sim \frac{a}{u_n^2}, \quad (2.37)$$

then speed of turbulent burning

$$u_t \sim u_n \sqrt{\frac{l w'}{a}} \quad (2.38)$$



or

$$u_t \sim u_n \sqrt{1 + \frac{lw'}{a}}$$

Thus, speed of turbulent burning at  $lw' \gg a$  is proportional to square root of pulsation velocity. Besides increase of speed of propagation of flame, there is increased also width of zone of flame

$$\delta_t \sim \frac{a_t}{u_t} \sim \sqrt{lw'}$$

Such considerations remain correct as long as mixing length is many times less than width of zone of flame, and as long as they refer to case of so-called small-scale turbulence. Here turbulent transfer is realized inside zone of flame, increasing its intensity.

This case was considered by Damköhler [49], investigating turbulent burning of propane-oxygen mixture by means of Bunsen burner. During turbulent regime of flow, which was established at  $Re > 2300$ , there appeared a diffuse cone, and width of zone of combustion was increased abruptly.

Calculated speed of burning in internal cone (Fig. 18) abruptly is increased compared to normal speed and, for example, at  $Re = 12 \cdot 10^3$ , exceeds the latter by three times. Thus the speed of propagation of flame, calculated along external cone, practically does not change.

For case of large-scale turbulence [50], [52], when mixing length is significantly larger than width of zone of flame, at first under influence of turbulence surface of flame is distorted, and then fresh mixture is broken up into separate volumes, which burn from their surface with speed  $u_n$ . This is schematically shown in Fig. 19. On the right, through section AA, proceeds fuel mixture, on the left, through section BB, pass out products of combustion. Average concentration of fresh gases in part between sections AA and BB is decreased, concentration of products of combustion is increased. Distance between sections AA and BB can be considered as thickness of front of turbulent flame. Burning inside such a zone is



transferred into fresh mixture by separate burning volumes, which accomplish pulsation motion.

If in the formula (2.36) time of burning is replaced by  $\tau \sim lw'$  then it turns out that

$$u_T \sim w'$$

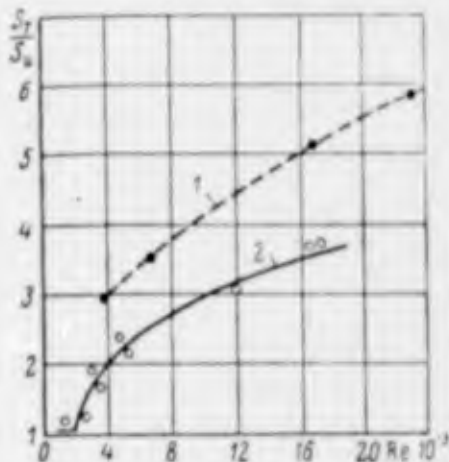


Fig. 18. Turbulent speed of burning as function of numbers Re (Damköhler). 1--theoretical curve, 2--experimental curve.

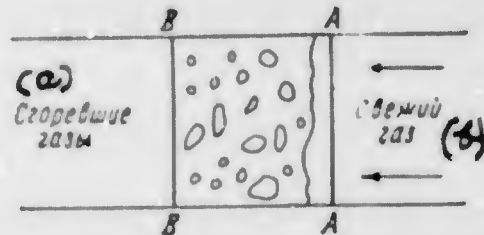


Fig. 19. Structure of turbulent flames (Shchelkin). KEY: (a) Burning gases; (b) Fresh gas.

In more general form dependence

$u_T = f(w')$ , taking into account influence of normal speed, can be obtained from considerations of dimension [61]. Thus

$$u_T = w' f\left(\frac{w'}{u_n}\right) \sim w'^{\alpha} u_n^{\beta} \quad (2.39)$$

where

$$\alpha + \beta = 1. \quad (2.40)$$

As Shchelkin shows [50], at  $w' \gg u_n$ , function  $f(w'/u_n)$  should tend to unity.

## 2. Ignition of Two-Phase Mixtures

The burning of gaseous, liquid and solid fuels in modern technology has assumed enormous proportions. This circumstance called into being a broad and new area of science — physics and chemistry of burning. The most substantial results in this area of science were obtained by Soviet scientists. Homogeneous burning was basically investigated by the Semenov School, heterogeneous burning was developed by the author of the present paragraph and his coworkers. Important contribution to the

matter of the development of our sciences in the area of heterogenous burning was also made by the Knorre school, which was the first to strive to introduce the theory to practice.

Actual flow of the processes of burning in technical apparatuses so far were complicated by secondary circumstances, the calculation of which greatly hampered the theoretical analysis of the problem. However in any process of the burning of fuel there are a number of general basic phenomena, which are connected with the nature of the process of burning and permit building the theory of the process regardless of the type of apparatus.

Without such a guiding theory one cannot intelligently or even qualitatively analyze the various phenomena of burning in technical apparatuses. Therefore, in the absence of such theories, the technology of heating apparatuses is doomed to extremely slow development, which is completely intolerable in terms of the progress of our country. The basic phenomena of homogeneous burning are the following; self-ignition, forced ignition, condition of normal propagation of flames, turbulent burning and detonation.

Basic mechanisms of homogeneous burning can be extended to burning of two-phase mixtures.

In the present chapter we will describe phenomenon of ignition of two-phase mixtures — gaseous oxidizer and liquid fuel — and will carry out analysis of stability of ignition of such a system.

Conditions for ignition of two-phase systems. From the theory of homogeneous burning it is known that conditions for ignition of gas mixtures are determined by equation of energy balance, equation of chemical kinetics and functional connection between temperature and composition of mixture. These three equations determine also conditions for ignition of a two-phase mixture.

Equation of energy balance in the given case is easy to construct. It is composed from energy of heating of gaseous phase, energy of heating of drops of

liquid, energy expended on evaporation, and, at last, energy released during burning of gaseous phase. Besides, it is necessary to take into account inequality of temperatures of gaseous phase and temperature of drops, which during evaporation of drops always is lower than temperature of remaining medium. Temperature of drops, while evaporation continues, remains constant. Upon ignition, temperature of gaseous medium should be functionally connected with concentration of fuel. We assume also that kinetics of burning is known at least in the most general form.

Thus, we will construct equation of energy balance under the condition that near source of ignition is formed zone of burning. Heating of gaseous mixture is determined by integral over the volume of zone of burning:

$$\int c_{v,g} \frac{dT}{dt} dv.$$

Heating of drops proceeds through heat exchange of drop with surrounding medium. We will designate by  $\varphi_1$ , the heat-transfer coefficient of a separate drop and will assume that it is identical for all drops. Further, by  $N$  we will designate number of drops per unit of volume and by  $S$  the surface of an individual drop. Then energy expended on heating of drops will be equal to

$$\int \varphi_1 S \Delta T N dv; \quad \Delta T = T - T_1.$$

If speed of burning is designated by function  $\Psi(T, z)$ , and by  $q$  is designated specific heat released during burning, then quantity of heat which will be released in zone of burning will to equal to

$$\int q \Psi dv.$$

Quantity of heat expended on evaporation (latent heat) is equal to

$$\int N q_1 \psi_1 dv.$$

Here by  $q_1$ , is designated latent heat of evaporation, and by  $\psi_1$ , — rate of evaporation.

Finally, heat obtained from external thermal source is equal to

$$\int \varphi \Delta T dS; \quad \Delta T = T - T_w.$$

Here,  $\varphi$  designates the heat transfer coefficient from the source to the medium.

Now the total thermal balance can be written in the form of the following integral equation:

$$\int c_{v,p} \frac{dT}{dt} dv + \int \varphi_1 S \Delta T N dv = \int q \psi dv - \int \varphi \Delta T dS. \quad (2.41)$$

We will designate derivative  $dT/dz$  by  $P$ . It has completely definite meaning during ignition of mixture. We will differentiate equation (2.41) with respect to variable  $z$ . Then we will consider that product  $C_{v,p}$  at the beginning of ignition weakly depends on concentration of combustible component  $z$ .

As a result we will have

$$\int c_{v,p} \frac{dP}{dt} dv + \int \varphi_1 S N dv = \int q \left( \frac{\partial \psi}{\partial z} + \frac{\partial \psi}{\partial T} P \right) dv - \int q_1 \frac{\partial \psi_1}{\partial T} P N dv - \int \varphi P dS. \quad (2.42)$$

We will differentiate now equation of kinetics with respect to temperature:

$$\frac{d}{dt} \frac{dz}{dt} = \frac{\partial \psi}{\partial T} + \frac{\partial \psi}{\partial z} \frac{1}{P}; \quad \frac{dz}{dt} = \psi$$

or

$$\frac{dP}{dt} = - \left( \frac{\partial \psi}{\partial T} R^2 + \frac{\partial \psi}{\partial z} P \right). \quad (2.43)$$

Inserting equation (2.43) into the equation (2.42), we have

$$\int \varphi_1 S P N dv = \int (c_{v,p} P + q) \left( \frac{\partial \psi}{\partial z} + \frac{\partial \psi}{\partial T} P \right) dv - \int q_1 \frac{\partial \psi_1}{\partial T} P N dv - \int \varphi P dS \quad (2.44)$$

or

$$\int \varphi P dS = \int (c_{v,p} P + q) \left( \frac{\partial \psi}{\partial z} + \frac{\partial \psi}{\partial T} P \right) dv - \int \left( \varphi_1 S + q_1 \frac{\partial \psi_1}{\partial T} \right) P N dv. \quad (2.44a)$$

If theorem of mean value is used, then this equality can be written as:

$$\overline{\varphi} \rho S = \overline{(c_{v,2} P + q) \left( \frac{\partial \psi}{\partial z} + \frac{\partial \psi}{\partial T} P \right) v} - \left( \overline{\varphi_1 S} + q_1 \frac{\partial \psi_1}{\partial T} \right) P N v.$$

Here line above functions indicates that mean value over the zone of burning is taken. We will designate  $\overline{P}$  by  $P_s$ . Then it is possible to represent certain mean values so that the following equality is valid:

$$\overline{(c_{v,2} P + q) \left( \frac{\partial \psi}{\partial z} + \frac{\partial \psi}{\partial T} P \right)} = \overline{(c_{v,2} P_s + q)} \times \\ \times \left( \overline{\frac{\partial \psi}{\partial z}} + \overline{\frac{\partial \psi}{\partial T}} P_s \right) \left( \overline{\varphi_1 S} + q_1 \frac{\partial \psi_1}{\partial T} \right) P_s N = \left( \overline{\varphi_1 S} + q_1 \frac{\partial \psi_1}{\partial T} \right) P_s N.$$

Taking these relationships into account, the last equality can be rewritten as:

$$\frac{\varphi S}{v} P_s = \overline{(c_{v,2} P_s + q) \left( \frac{\partial \psi}{\partial z} + \frac{\partial \psi}{\partial T} P_s \right)} - \left( \overline{\varphi_1 S} + q_1 \frac{\partial \psi_1}{\partial T} \right) P_s N. \quad (2.45)$$

This relationship is also assumed as the basis of our reasoning; relative to the conditions of ignition of two-phase mixtures.

Let us examine the slow heating of two-phase mixtures. In this case it is possible to consider the correct inequalities

$$\frac{\partial \psi}{\partial T} P_s \gg \frac{\partial \psi}{\partial z}; \quad \overline{c_{v,2} P_s} \ll q.$$

Taking into account these inequalities, equation (2.45) can be represented in this form:

$$\frac{\varphi S}{v} = q \frac{\partial \psi}{\partial T} - \left( \overline{\varphi_1 S} + q_1 \frac{\partial \psi_1}{\partial T} \right) N \quad (2.46)$$

or

$$\frac{qv}{\varphi S} \frac{\partial \psi}{\partial T} - \left( \overline{\varphi_1 S} + q_1 \frac{\partial \psi_1}{\partial T} \right) \frac{Nv}{\varphi S} \approx 1. \quad (2.46a)$$

Fast heating of substance will lead to formation and movement of zone of burning. For that case value of  $P_s$  will be such that there should be fulfilled inequalities of the following form:

$$\frac{\partial \psi}{\partial T} P_s \gg \frac{\partial \psi}{\partial z}; \quad \overline{c_{v,2} P_s} \gg q.$$

Considering these inequalities, to equation (2.45) it is possible to impart the following form:

$$\frac{\varphi S}{V} = \overline{c_p} \frac{\partial \psi}{\partial T} P_s - \left( \varphi_1 S + q_1 \frac{\partial \psi_1}{\partial T} \right) N, \quad (2.47)$$

from this follows

$$P_s = \frac{\varphi S}{V} \frac{1}{\overline{c_p} \frac{\partial \psi}{\partial T}} + \frac{\left( \varphi_1 S + q_1 \frac{\partial \psi_1}{\partial T} \right) N}{\overline{c_p} \frac{\partial \psi}{\partial T}}. \quad (2.47a)$$

We will transform quantity  $P_s$ . It can be written as:

$$P_s = \frac{\Delta T}{\Delta z} = \frac{\Delta T}{\tau} \frac{\tau}{\Delta z} = \frac{\Delta T}{\tau \psi} = \frac{\Delta T}{\Delta n} \frac{\Delta n}{\tau} \frac{1}{\psi}.$$

Here, by  $\tau$  is designated time of formation of zone of burning, and by  $\Delta n$  -- increase of normal during the time of formation of zone of burning. Quantity  $\Delta n / \tau$  is a measure of speed of displacement  $g$  of zone of burning. Temperature gradient is ratio of thermal flux to average coefficient of thermal conductivity of medium. Speed of displacement of zone of burning and thermal flux  $Q$  will be directed in the same direction. Therefore, we have

$$P_s = \frac{Q}{\lambda} g \frac{1}{\psi}. \quad (2.48)$$

If this magnitude is inserted in equality (2.47a), we will obtain

$$g = \frac{\varphi S}{V} \frac{\overline{\lambda \psi}}{Q} \frac{1}{\overline{c_p} \frac{\partial \psi}{\partial T}} + \frac{\left( \varphi_1 S + q_1 \frac{\partial \psi_1}{\partial T} \right) N \overline{\lambda \psi}}{\overline{c_p} \frac{\partial \psi}{\partial T} Q}. \quad (2.48a)$$

Ratio  $\frac{\partial \psi}{\partial T} / \psi$  can be replaced accordingly by the selected derivative

$$\frac{\partial \lg \psi}{\partial T}.$$

Designating mean value of coefficient of thermal diffusivity of the medium by  $\bar{a}$  equality (2.48a) can be represented in the following form:

$$g = \frac{\varphi S}{v} \frac{\bar{a}}{Q} \frac{1}{\frac{\partial \lg \psi}{\partial T}} + \frac{\left( \varphi_1 S + q_1 \frac{\partial \psi_1}{\partial T} \right) \bar{a} N}{\frac{\partial \lg \psi}{\partial T} Q}. \quad (2.48b)$$



Ratio  $v/S$  is thickness  $d$  of zone of burning. Therefore there can be written

$$\frac{v}{S} = d = g\tau.$$

But for time of formation of zone of burning,  $\tau$  the following equality is correct:

$$\int \psi dt = \bar{\psi}\tau = M.$$

Considering what has been said, we will have

$$\frac{v}{S} = g \frac{M}{\bar{\psi}}.$$

Inserting this relationship into the formula (2.48b), we obtain

$$g^2 = \frac{\bar{\psi} a}{Q M \frac{\partial \lg \psi}{\partial T}} + \frac{\left( \varphi_1 S + q_1 \frac{\partial \psi_1}{\partial T} \right) \bar{a} N}{Q \frac{\partial \lg \psi}{\partial T}} g. \quad (2.49)$$

Thermal fluxes, expressed by heat-transfer coefficient and average coefficient of thermal conductivity, are equal to each other. Therefore we will have:

$$Q = \bar{\varphi} \Delta T = \lambda \frac{\Delta T}{\Delta n}.$$

Considering this, equality (2.49) will be rewritten as

$$g^2 = \frac{\bar{a} \lambda}{\Delta T M \frac{\partial \lg \psi}{\partial T}} + \frac{\left( \varphi_1 S + q_1 \frac{\partial \psi_1}{\partial T} \right) \bar{a} N}{Q \frac{\partial \lg \psi}{\partial T}} g. \quad (2.49a)$$

But the following identity is correct:

$$\Delta T = \frac{\Delta T}{\Delta n} \frac{dn}{\lambda} = \frac{Q}{\lambda} g\tau,$$

therefore we have

$$g^3 = \frac{\bar{a} \lambda}{M^2 Q \frac{\partial \lg \psi}{\partial T}} + \frac{\left( \varphi_1 S + q_1 \frac{\partial \psi_1}{\partial T} \right) \bar{a} N}{Q \frac{\partial \lg \psi}{\partial T}} = g^2. \quad (2.49b)$$

Thus, we have obtained a formula for speed of displacement of zone of burning in two-phase mixtures during constant thermal flux from source of ignition.

Speed of burning of gaseous phase can be represented as

$$\psi = F(T) f(z).$$

therefore the following equation is correct:

$$\frac{\partial \lg \psi}{\partial T} = \frac{\partial \lg F}{\partial T}.$$

Now equation (2.49b) can be rewritten in its final form:

$$g^3 = \frac{\bar{a}\bar{\psi}\bar{\lambda}}{M^2 Q \frac{\partial \lg F}{\partial T}} + \left( \bar{\tau}_1 S + q_1 \frac{\partial \bar{\psi}_1}{\partial T} \right) \frac{\bar{a}N}{Q \frac{\partial \lg F}{\partial T}} g^2. \quad (2.50)$$

Physical meaning of components in this expression is explained very simply. In reality, in the absence of liquid drops, speed of displacement of zone of burning  $g_0$  will be equal to

$$g_0^3 = \frac{\bar{a}\bar{\psi}^2}{M^2 Q \frac{\partial \lg F}{\partial T}}.$$

In the case when speed of burning will be near to zero, zone of evaporation will be transferred with speed  $g_1$ . As follows from formula (2.50), it will be equal to

$$g_1 = \frac{\bar{\tau}_1 S + q_1 \frac{\partial \bar{\psi}}{\partial T} \bar{a}N}{Q \frac{\partial \lg F}{\partial T}}$$

Considering what has been said, formula (2.50) can be rewritten in the following form:

$$g^3 = g_0^3 + g_1 g^2. \quad (2.50a)$$

Stability of ignition of two-phase systems. We will explain, under what conditions equation (2.50a) has real roots and how many of them there are.

We reduce the shown equation to canonical form. With this purpose let us assume

$$g = y + \frac{g_1}{3}.$$

We will substitute this expression into the equation (2.50a); then we will have

$$y^3 - \frac{g_1^2}{3} y - 2 \left( \frac{g_1^3}{27} + \frac{g_0^3}{2} \right) = 0. \quad (2.51)$$

As it is known, canonical cubic equation has following form:

$$y^3 + 3py + 2q = 0.$$

Consequently, in our case there will be correct the identities

$$p = -\frac{g_1^2}{9}; \quad q = -\frac{g_1^3}{27} + \frac{g_0^3}{2}.$$

Condition of one real root and two imaginary roots is written in the form of the following:

$$p^3 + q^2 > 0; \quad \left( \frac{g_1^3}{27} + \frac{g_0^3}{2} \right)^2 - \frac{g_1^6}{27^2} > 0.$$

from this follows

$$g_0^3 \left( \frac{g_1^3}{27} + \frac{g_0^3}{4} \right) > 0. \quad (2.52)$$

Quantity  $g_0$  is always positive. Consequently, inequality (2.52) will be observed only under the condition:

$$\frac{g_1^3}{27} + \frac{g_0^3}{4} > 0. \quad (2.52a)$$

At positive value of quantity  $g_1$ , we will have one real root and two imaginary. But quantity  $g_1$  is equal to

$$g_1 = \frac{\left( \tau_1 S + q_1 \frac{\partial \psi_1}{\partial T} \right) a N}{Q \frac{\partial \lg F}{\partial T}}.$$

For further analysis we will transform expressions for  $g_1$ . In the steady-state case, quantity of heat supplied to one drop can be placed equal to latent heat released per unit of time. In other words, there should be observed the equality

$$\tau_1 S (T - T_k) = q_1 \psi_1.$$

Considering this, we obtain expression for speed  $g_1$

$$g_1 = \frac{\tau_1 S (T - T_k) N a}{(T - T_k) Q \frac{\partial \lg F}{\partial T}} \left[ 1 + \frac{\partial \lg \psi_1}{\partial T} (T - T_k) \right].$$

Let thermal source of ignition give heat exactly in the amount required to evaporate drops. In this case we will have

$$\varphi_1 S(T - T_k) N v = Q S.$$

Considering this, last formula takes the form

$$g_1 = \frac{\bar{a} S}{v(T - T_k) \frac{\partial \lg \bar{F}}{\partial T}} \left[ 1 + \frac{\partial \lg \psi_1}{\partial T} (T - T_k) \right].$$

But ratio  $v/S$ , as we have seen above, is equal to

$$\frac{v}{S} = d = g = g \frac{M}{\psi},$$

therefore, we have

$$g g_1 = \frac{\bar{a} \bar{\psi}}{M(T - T_k) \frac{\partial \lg \bar{F}}{\partial T}} \left[ 1 + \frac{\partial \lg \psi_1}{\partial T} (T - T_k) \right]. \quad (2.53)$$

Factor  $M$  in this formula exactly coincides with first component of formula (2.49a), which is equal to  $g_0^2$ , if in this case difference  $\Delta T$  will be equal to difference  $(T - T_k)$ . In the general case, these differences are not equal to each other. We will designate by  $\gamma$  the ratio

$$\frac{\Delta T}{T - T_k} = \gamma.$$

Taking it into consideration formula (14) can be presented in the following form:

$$g g_1 = \gamma g_0^2 \left[ 1 + \frac{\partial \lg \psi_1}{\partial T} (T - T_k) \right]. \quad (2.53a)$$

We will insert the obtained value for speed  $g_1$  into equality (2.50a). As a result we obtain

$$g^3 = g_0^3 + \gamma g_0^2 \left[ 1 + \frac{\partial \lg \psi_1}{\partial T} (T - T_k) \right] g. \quad (2.54)$$

From this cubic equation, it is clear that it has canonical form.

For equation (2.54) we have

$$3P = -\gamma g_0^2 \left[ 1 + \frac{\partial \lg \psi_1}{\partial T} (T - T_k) \right]; \quad 2q = g_0^3.$$

Condition of existence of one real root and two imaginary roots will look like:

$$\frac{g_0^6}{4} - \frac{\gamma^3 g_0^6 \left[ 1 + \frac{\partial \lg \psi}{\partial T} (T - T_*) \right]^3}{27} > 0$$

or

$$\frac{1}{4} - \frac{\gamma^3 \left[ 1 + \frac{\partial \lg \psi_1}{\partial T} (T - T_*) \right]^3}{27} > 0. \quad (2.55)$$

Condition of three real roots will have following form:

$$\frac{1}{4} - \frac{\gamma^3 \left[ 1 + \frac{\partial \lg \psi_1}{\partial T} (T - T_*) \right]^3}{27} = 0. \quad (2.55a)$$

Obviously, both cases are possible. First condition will correspond to stable ignition; the second, conversely, to unstable ignition.

As can be seen from the presented formulas, both cases will depend on the absolute value of rate of evaporation of drops and on the ratio

$$\frac{\Delta T}{T - T_*} = \gamma.$$

Quantity  $\frac{\partial \lg \psi}{\partial T} (T - T_*)$  can be interpreted increment of speed of evaporation of drops due to temperature gradient at surface of drops. If this quantity is positive and larger than unity, then at all values of quantity  $\gamma$  there will be observed stable burning. If this quantity is positive and less than unity, then stable ignition will exclusively depend on absolute value of quantity  $\gamma$ . This quantity is equal to ratio of jump in temperature in zone of burning to jump in temperature near evaporating drop. Therefore, in accordance with physical meaning, its least value is equal to unity. In reality, both of these jumps hardly become equal, although this does not contradict the logic of things.

The ideas which have been discussed allow us to describe ignition and burning of two-phase mixtures in all their variety.

### 3. Burning of Atomized Fuel

Elementary schemes of turbulent burning of a homogeneous mixture very rarely are met in technical mechanisms. The most wide-spread method of supplying of

components in different combustion chambers is separate supply of oxidizer and fuel. Fuel components will move into zone of burning in broken-up form, but processes of fuel carburation and burning occur in the chamber itself and proceed almost simultaneously.

Process of burning occurs in a zone which is broken up into a large number of miniature regions of burning. Rate of process is limited by hydrodynamic factors, and in the first place by mixing. Such a form of burning, when rate of burning entirely is determined by mass transfer, is called micro-diffusion turbulent burning. It is observed in those cases, when chemical reactions due to high temperatures occur practically instantly and the process is limited by fuel atomization. This form of burning is observed in all motors, where there exists separate supplying of components.

In a number of motors, due to their imperfection, burning occurs in an intermediate region. Total rate of such a process is in complex dependence on hydrodynamic, as well as on kinetic factors. For a process proceeding in the diffusion region, time of combustion is equal to time of mixing. If we designate average dimension of broken-up volumes of fuel and oxidizer by  $\delta$ , then time of mixing will be

$$\tau = \frac{\delta^2}{D}, \quad (2.56)$$

where  $D$  -- diffusion coefficient.

If mixing occurs by means of turbulent diffusion, then instead of diffusion coefficient it is possible to present coefficient of turbulent exchange

$$\tau = \frac{\delta^2}{lw'}. \quad (2.57)$$

When mixing occurs by means of turbulent diffusion. Speed of burning will be

$$v \sim \frac{lw'}{\delta}. \quad (2.58)$$

When the scale of break-up is on the same order as the scale of turbulence, then formula (2.58) gives

$$v \sim w', \quad (2.59)$$



i. e., speed of burning equals pulsation velocity.

At present there are a number of investigations which show that burning of atomized fuel is the burning which proceeds in the diffusion region.

Experimental study of influence of physical and chemical factors on process of burning of atomized fuel presents large difficulties. Therefore, almost all investigations pertaining to this problem were conducted under conditions, where influence of a number of factors was excluded. In particular, investigation of rates of combustion of different fuels and individual hydrocarbons were conducted with separate drops. Flow around spheres was studied. These spheres were liquid drops or drops suspended on filaments. Photography of burning drop in time, allows the establishment of influence of different factors on rate of combustion.

In investigations [54]--[58], experimental results are obtained in form of direct dependence of diameter of drop on time. Typical dependence of diameter of drop on time is presented in Fig. 20; it is possible to present the following equality:

$$d^2 = d_0^2 - K't, \quad (2.60)$$

where  $d$  -- diameter of drop;

$d_0$  -- initial diameter of drop;

$t$  -- time from moment of ignition;

$K'$  -- constant of evaporation, not dependent on dimension of drop and characterizing the considered fuel system.

This constant serves for comparison of combustion of drops of different fuels having arbitrary dimensions. Quantity  $K'$  is determined directly from angle of slope of curve  $d = f(t)$  (Table 5).

Measurement of rate of combustion of drops at temperatures to  $900^\circ \text{C}$  again showed that rate of combustion is proportional to diameter of drop [55].

Investigations of rate of combustion of drop in flame are strongly hampered by turbulence and also by different speeds of motion of drops of different diameters.

Table 5. Experimental Values of  $K'$  for Different Fuels

Топливо (a)	$K'$ в $\text{см}^2/\text{сек}$ (b)
(c) Этиловый спирт	0,0081
(d) Толуол	0,0066
(e) Бензол	0,0099
(f) n-гептан	0,0084

KEY: (a) Fuel; (b)  $K'$  in  $\text{cm}^2/\text{sec}$ ;  
 (c) Ethyl alcohol; (d) Toluene;  
 (e) Benzene; (f) n-heptane.

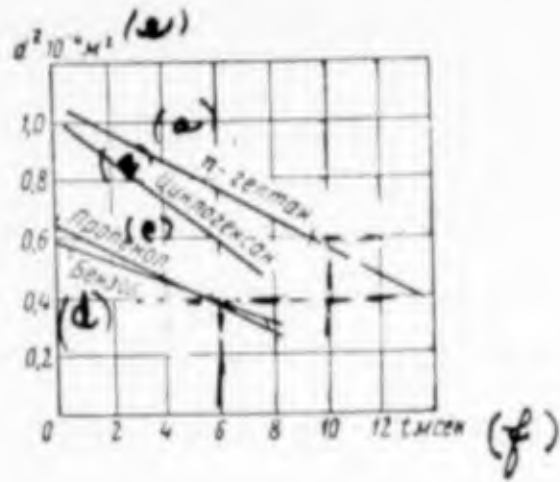


Fig. 20. Rate of combustion of fuel stream as a function of diameter of drops [58].  
 (a) n-heptane; (b) Cyclohexane; (c) Propenol; (d) Benzene; (e)  $\text{m}^2$ ; (f)  $\text{m sec}$ .

Estimation of values of  $K'$  during burning of group of drops of various sizes in high-speed turbulent flow was accomplished in work [57].

Obtained values of  $K'$  allow us to make comparison with numerous experimental values for a number of substances under different conditions. For drops  $d = 80 - 111 \mu$ , value of  $K'$  is 1.5 - 2 times lower than values obtained for single drops, but coincides with data corresponding to experiments with groups of drops.

Determination of constant  $K'$  allows us to estimate not only rate of combustion of atomized fuel, but also allows us to establish those critical diameters with which burning changes from the diffusion region to the kinetic region.

In Fig. 20 is presented the dependence of diameter of a drop in a flame, obtained at uniform atomization. Here also the dependence has a linear character.

Thus, in spite of evident limitedness of investigations of burning of separate drops and of fuel of a flame, it is possible to establish that physical processes appearing during burning of atomized fuel basically determine the essence of this process.

#### 4. Elements of Theory of Detonation

Lately, in a number of investigations it has been shown that with a certain idealization, processes of combustion in liquid-fuel rocket engine are supported by

hydrodynamic theory of detonation. In connection with this, below are expounded elements of theory of detonation propagation of a flame.

In 1881, in France, at the same time Berthelot and Vieille, and also Mallar and Le Chatelier discovered the phenomenon of detonation — propagation of flame with velocity of several kilometers per second.

Main properties of detonation waves, distinguishing them from a whole series of other forms of propagation of flame, are expressed in the following classical traits.

1. Velocity of detonation wave almost does not depend on initial physical parameters (pressure, temperature) of the gas mixture and is a physicochemical constant, characterizing a given gas mixture.

2. Propagation of detonation is accompanied by movement of shock wave through unburned gas.

3. During detonation, combustion products upon completion of chemical reaction have higher density than fresh mixture, and move in direction of propagation of detonation with velocity 1--1 1/2 km/sec.

4. Pressure in detonation wave by 15--30 times exceeds the initial pressure.

5. In detonation wave, as well as in shock wave, change of state after compression depends on change of entropy of system.

Steady-state velocity of detonation remains constant, and within wide limits does not depend on material and diameter of pipe. It is determined exclusively by composition of explosive mixture, its temperature and pressure (influence of latter is insignificant). As compared to ordinary burning, during detonation there is developed significantly higher pressure which explains its strong destructive action.

Contemporary hydrodynamic theory of detonation allows us with great accuracy to calculate velocity of propagation of detonation and state of combustion products in detonation wave. Thus, for calculation it is necessary to know only thermochemical characteristics of mixture: heat of combustion, composition and heat

capacity of reaction products.

Chemical reaction rate in detonation wave appears immaterial for its velocity, if only the rate of reaction is sufficiently great, so that detonation in general takes place. Theory of velocity propagation of detonation has been far advanced, compared with theory of normal propagation of flame.

Huge velocities of propagation of detonation indicate that in the given case we deal with a mechanism which is completely different from mechanism of normal propagation of flame; in this type of combustion, the combustible gas mixture is set fire by the shock wave of pressure, and not by means of thermal conduction.

One of first who expressed such a point of view was Michelson, who in his known dissertation [59] gave a theoretical analysis of the phenomenon of detonation. As distinguished from usual shock waves, which rapidly die out and degenerate into sound waves, detonation waves do not degenerate, but are propagated for an arbitrarily long time with constant speed.

The steady-state regime of a detonation wave is supported by energy liberated as a result of chemical reaction. Theory of detonation very successfully was developed by Zel'dovich and Shchelkin. Investigations carried out by them explained a number of phenomena which are observed during detonation; here also was created contemporary theory of detonation.

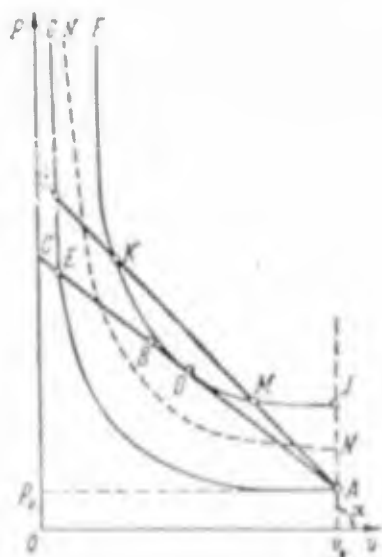
Lately there has been noted a tendency to explain with the help of the theory of detonation types of combustion with speed equal to and exceeding the speed of sound, which have been observed in many technical mechanisms.

Process of burning of fuel mixture is accompanied by movement of gas before front of flame; layers of gas adjacent to walls, due to deceleration change profile of velocity of flow, which in its turn increases speed of burning. As acceleration of flame increases, amplitude of wave increases, and in compressed layers of gas before the front, as a final result, temperature will reach the temperature of self-ignition of the mixture.

Further acceleration of motion of gas leads to the case when velocity of shock wave reaches steady-state velocity of detonation. Qualitative picture of appearance of detonation must be supplemented by the fact that in detonation wave, as distinguished from shock wave, energy separated in zone of combustion is source of constancy of velocity of propagation of flame.

Width of zone of combustion of detonation wave is wider than zone of usual shock wave. Therefore, it is possible to carry out clear division into two regions: in one the gas is compressed, but in it there still is no chemical reaction; in the another the reaction has mainly already been completed.

It is easy to construct an equation of conservation of mass, momentum, energy and, using equation of state, obtain equation of curve lying in plane  $p-v$  (Fig. 21).



Curve AEG corresponds to the case when quantity of heat  $Q_{\text{ch}}$ , which is released as a result of chemical reaction equals zero. This curve is called adiabatic line of Hugoniot for shock wave, but curve FDJ corresponds to case  $Q_{\text{chem}} \neq 0$  and is adiabatic line of Hugoniot for detonation wave.

Velocity of detonation is determined

Fig. 21. Adiabatic curve of Hugoniot for shock and detonation waves.

by equation

$$D = mv_0 = v_0 \sqrt{\frac{p_1 - p_0}{v_0 - v_1}}, \quad (2.61)$$

where

$m$  -- mass of gas, following per unit of time through unit of surface of wave;

$p_0$ ;  $v_0$ ;  $p_1$  and  $v_1$  -- pressure and specific volume of gas of fresh mixture and reaction products respectively.

Point D of adiabatic curve of Hugoniot JMKE, in which secant AK becomes a tangent, corresponds to maximum of entropy on straight line AC and minimum possible



velocity of detonation.

Velocity of propagation of detonation relative to reaction products equals local speed of sound. This property of the detonation wave distinguishes from usual shock wave, velocity of propagation of which, relative to compressed gas, is always smaller than speed of sound.

Theory of detonation, obtained mainly from thermodynamic considerations, could not explain many experimental facts. In particular, it was impossible to explain with the help of this theory the sensitivity of a certain fuel mixture to detonation.

Experimental results of a whole series of works gave the possibility to approach the theory of detonation from new concepts.

Zel'dovich Kompaneyets [30], [60] by means of introduction of new qualitative concepts concerning flow of reaction in detonation wave created a new theory of detonation, connecting gas-dynamic phenomena of detonation with chemical kinetics. Analysis of process, considering losses due to heat transfer and friction during the reaction, was carried out by Zel'dovich; it showed the following: when in the gas, release of heat from the reaction is compensated by losses, there is realized a fundamental property of detonation — velocity of propagation of detonation wave becomes equal to the local speed of sound. This remarkable property of detonation wave ensures its stability.

Steady-state propagation of detonation and detonation limits, strongly depend on time and chemical reaction rate.

In works of Rivin [61], [62], and also of Rivin and Sokolik [63], for the first time there were carried out investigations of limits of different fuel mixtures and their detonation ability. Rivin and Sokolik, by means of introduction of small impurities into the explosive mixture, changed ability of fuel mixtures to detonate.

By mixing to a non-detonating mixture of carbon monoxide with air, 1.3% H<sub>2</sub>, they obtained in this mixture stable detonation. Analogous action on detonation is



rendered by a small impurity (0.3%) of acetylene. Action of additions of hydrogen and acetylene is explained by the fact that in their presence is increased abruptly rate of oxidation of carbon monoxide.

Significant influence on position of detonation limits is rendered by the conditions under which detonation wave is propagated. Thus, in detonation wave, as well as during combustion of majority of usual fuel mixtures, there is a period of delay of ignition, which is connected with preparation of the mixture for chemical reaction.

However, role of kinetic parameters becomes noticeable only near limits of propagation of flame and, obviously, in the case of investigation of stable steady-state detonation propagation of flame, they can be omitted during approximate analysis.

Strict consideration of these questions presents independent interest and is beyond the scope of this book [60].

## CHAPTER III

### KINETICS OF CHEMICAL REACTIONS IN FLAME

#### Section 1. Structure of Front of Flame

During burning of fuel mixture, the flame is a zone which is separated from original mixture and final products of reaction. During the time of transformation of fuel mixture, chemical energy of original mixture is turned into thermal energy. Knowing the state of the original fuel mixture it is possible, by using thermodynamic methods, to calculate composition of combustion products both with and without consideration of dissociation. If in the system temperature is above 1800°--2000° K, dissociation of triatomic combustion products becomes noticeable, and during accurate calculations its consideration is mandatory.

Without touching simultaneously upon the entire range of complicated processes occurring in the flame it is necessary to explain what is the width of the zone of the flame, time reacting substances remain in it, speed of propagation of flame relative to combustion products.

Michelson [59], for the first time, applied the solution of Hertz concerning a thermal wave before a heated surface, moving with constant speed, to a flame. This solution has the form

$$T = T_0 + Be^{\frac{-xx}{v}} \quad (3.1)$$

where  $T_0$  -- initial temperature of substance in undisturbed thermal wave;

B -- constant, determined from boundary conditions;

u -- speed of flame;

$\kappa$  -- coefficient of thermal diffusivity.

One should note that the solution of Michelson is applicable to the zone of preliminary heating, where there is still no chemical reaction or corresponding heat release (Fig. 22). As the scale of width of the zone, let us take the distance at which heating-up increases by  $e$  times ( $e=2.7$ ):

$$l = \frac{\kappa}{u} = \frac{\lambda}{c_p \rho u} \quad (3.2)$$

Zel'dovich [4] calculated width of zone of flame for the most slowly and rapidly burning explosive mixtures. Results of calculation are presented in Table 6.

Table 6.

(a) Горючая смесь	(b) Скорость пламени $u$ см/сек	(c) Ширина $l$ см	(d) Время пребывания $\tau = \frac{l}{u}$ сек.
(e) (6% $\text{CH}_4 + 94\%$ воздуха)	5	0.06	$4 \cdot 10^{-3}$
(f) (2H <sub>2</sub> +O <sub>2</sub> ) средняя смесь	1000	0.0003	$10^{-7}$

KEY: (a) Fuel mixture; (b) Speed of flame cm/sec;  
(c) Width cm; (d) Time of stay  $\frac{l}{u}$  sec; (e) Air;  
(f) Detonating mixture.

From numbers presented in the last column of Table 6, it is clear that the time of stay of the substance in the flame is a little longer than the time of free path of a molecule in the gas. This is in full conformity with the fact that the reactions, in view of high activation energy and nature of complex flow, need a large number of collisions for every collision leading to a chemical reaction.

As a result of chemical reaction, there simultaneously change concentrations of reacting substances and temperature. These parameters change also in the zone where chemical reaction is absent. Composition changes due to diffusion, and temperature changes due to thermal conduction. In the case of near molecular weights of original substances and combustion products, diffusion coefficient and coefficient

of thermal diffusivity should be near to each other. It is possible to show that in a flame, composition and temperature of gases change as if the chemical reaction proceeded adiabatically, without heat exchange and mass exchange with subsequent neighboring layers.

In the zone of flame is maintained constancy of sum of thermal and chemical energy. Increase thermal energy due to heating of mixture is compensated by loss of chemical energy from original substances, which are carried away by diffusion.

Zel'dovich [30] considered three cases of homogeneous burning.

First case  $D = \kappa$  (diffusion coefficient equal coefficient of thermal diffusivity). If molecular weight of reacting substances and reaction products are close, then diffusion coefficient will correspond in order of magnitude to coefficient of thermal diffusivity. In this case reaction proceeds adiabatically, i.e., heat exchange and mass exchange with neighboring layers is absent (Fig. 23a).

Second case  $D > \kappa$ . This case is applicable to lean hydrogen-air mixtures, when diffusion coefficient is larger than the coefficient of thermal diffusivity. Hydrogen diffuses but of the still unheated layers and enthalpy has its minimum value (Fig. 23b).

Third case  $D < \kappa$ . During burning of mixtures of substances with large molecular weight, for example benzene with air, heat is propagated rapidly and heating of mixture occurs much faster than benzene diffuses into zone of flame. Here enthalpy has its maximum value (Fig. 23c).

Chemical reactions in flame occur under the conditions, when original mixture is heated due to thermal conduction. Second important factor is change of composition as a result of diffusion from neighboring layers. Action of these two important factors leads to dilution of original mixture by products of chemical reaction in flame.

We will indicate that the distinctive trait of high-temperature kinetics of chemical reactions in flames is that fast growth of temperature prevents retarding

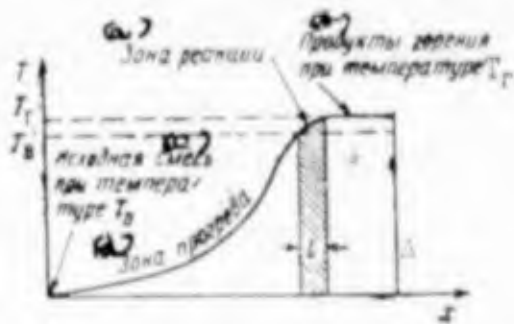


Fig. 22. Preheating zone, zone of burning end zone of burnt gas.  
 KEY: (a) Zone of reaction; (b) Combustion products at temperature; (c) Original mixture at temperature, (d) Zone of heating.

stages, while during self-ignition, period of accumulation of heat and active centers retards development of process in flame.

On temperature range from initial to  $T_T$ , we have change of concentration of reacting components with corresponding change of temperature.

Under the conditions of relative change in the front of the flame of concentration

of reacting substances and temperature, chemical reaction rate changes.

One of the main problems of investigation of kinetics of reactions at high temperatures is establishment of connection between speed of propagation of flame and chemical reaction rate in it. For clarification of kinetics of process of burning of homogeneous gas mixtures, we should in detail consider the narrow layer in which chemical reaction occurs, i.e., transformation of original fuel mixture into combustion products.

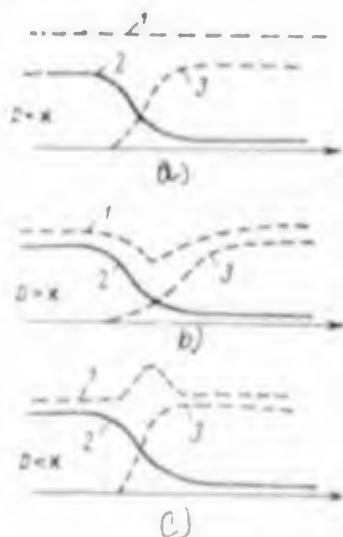


Fig. 23. Three case of homogeneous burning.  
 1--enthalpy, 2--temperature, 3-- concentration of fuel (Zel'dovich).

In Chapters I and II we established that propagation of flame occurs due to relay heat transfer from layer to layer. Simultaneously with heat transfer there is realized process of mass transfer, i.e., diffusion. Fuel components diffuse into zone of burning, where there occurs transformation of the fuel under the conditions of intense heat release.

Chemical reaction in flame occurs in

narrow range of temperatures  $\theta$  (Fig. 24). Thickness of chemical zone of flame  $\delta_T$  is less than total thickness  $\delta = \delta_0 + \delta_T$ , where  $\delta_0$ --zone of preliminary heating.

Heat is brought into zone of preliminary heating by thermal conduction from zone of chemical reaction and, correspondingly, fuel components undergo diffusion from zone of preliminary heating into zone of reaction. Fuel mixture basically reacts in zone of chemical reaction in range of temperatures  $T_r \rightarrow \theta$ .

In zone of preliminary heating  $\delta - \delta_p$ , which is considerably larger than zone of reaction, chemical reaction practically does not occur.

Heat, proceeding from hot part of flame into zone of heating due to thermal conduction, should be equal to the heat which is necessary for heating of original fuel mixture to a definite temperature:

$$\lambda \frac{dT}{dx} = u_0 \rho c_p (T_0 - T_0) \quad (3.3)$$

It is possible to write an approximate equation for temperature gradient in zone of flame

$$\frac{dT}{dx} \approx \frac{T_0 - T_0}{\delta} \quad (3.4)$$

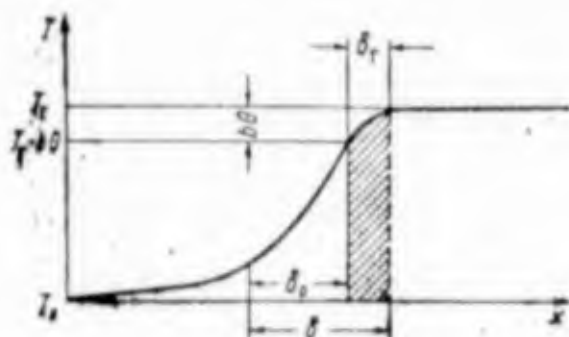


Fig. 24. Diagram chemical reaction in flame.

By substituting equation (3.4) into (3.3), we obtain for width of zone of flame the following expression:

$$\delta \approx \frac{\lambda}{u_0 \rho c_p} \quad (3.5)$$

since

where  $\kappa$  -- coefficient of thermal diffusivity

$$\delta \approx \frac{\kappa}{u_0} \quad (3.6)$$



It is not without interest also to estimate order of time of heat-up of fuel mixture in layer  $\delta$  ; approximately it can be written as

$$t_{\text{heat-up}} = \frac{\delta}{u_n} = \frac{x}{u_n^2} \quad (3.7)$$

From these equations it follows that the higher the normal speed of propagation of flame, the less the width of the zone and the time of heat-up.

Contemporary concepts of the theory of burning give grounds to assert that fast chemical reaction occurs in zone of the highest temperature, approaching the theoretical temperature of burning. We will designate temperature of burning by  $T_r$ , initial temperature by  $T_0$ ; range of temperature in which reaction mainly occurs equals  $T_r$  to  $(T_r - \theta)$ , where

$$\theta = \frac{RT_r^2}{E} \quad (3.8)$$

$E$ --activation energy of reaction.

In all real processes of burning

$$E \gg RT_r \quad \text{and} \quad \theta \ll T_r - T_0$$

Heating of unburned gas from  $T_0$  to  $T_r - \theta$  occurs mainly due to thermal conduction. In the zone of heating, release of heat due to the reaction is small, but depth of penetration of heat as a function of temperature can be determined from the following equation:

$$\frac{dx}{dT} = \frac{\lambda}{u_n \rho_0 c_p (T - T_0)} \quad (3.9)$$

where  $x$  -- depth of penetration of heat;

$\lambda$  -- thermal conductivity of fuel mixture;

$\rho_0$  -- density;

$c_p$  -- average heat capacity in range of temperatures ( $T_0$ -- $T$ );

$T_0$  -- initial temperature.

By integrating equation (3.9), Michelson determined depth of penetration of heat and width of pre-reaction zone under the assumption of constancy of  $\lambda$  and  $C$  (quantity  $u_n$  is constant along the entire front).

Distribution of temperatures in zone of heating of gases, in which chemical reaction rate is still small, is determined by equation

$$T - T_0 = (T_r - T_0) e^{-\frac{c_p \rho_0 u_n x}{\bar{\lambda}}}, \quad (3.10)$$

where  $\bar{\lambda}$  -- average thermal conductivity in range of temperatures  $T_0$ -- $T$ .

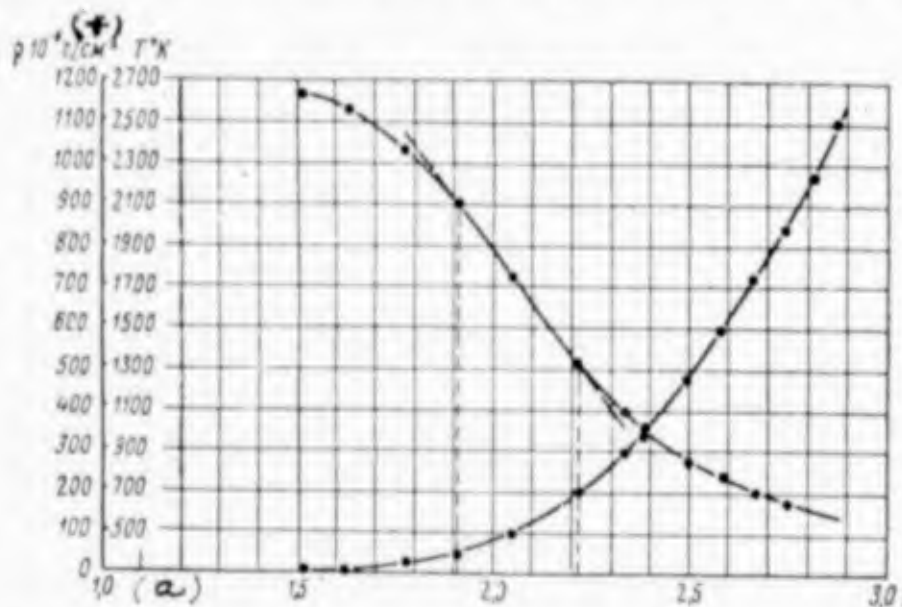


Fig. 25. Change of temperature and density over the depth of the pre-reaction zone of the flame.  
KEY: (a) Depth of penetration of heat in mm; (b) g/cm<sup>2</sup>.

Considering boundary of zone of heating to be a plane, where temperature compared with the initial is increased by 0.01 ( $T - T_0$ ). Damköhler obtains for width of this zone

$$x \approx \frac{5\bar{\lambda}}{c_p \rho_0 u_n}. \quad (3.11)$$

Based on concepts developed above, Zarembo and Zel'dovich [64] investigated structure of Bunsen flame, using equation (3.9). They showed that in Bunsen flame of methane air mixture, boundaries of sharp change of density of unburned gas correspond to temperatures which are equal approximately to 400°--700° K (Fig. 25). They determined further the width of this zone and found distribution of temperatures along normal to surface of front of flame.

For checking results of calculation, Zarembo and Zel'dovich conducted experimental investigation of structure of flame by method of shadow photography of Bunsen cone.

Sharpness of boundaries of zone of strong change of density of reacting gas mixture makes it possible to establish that during passage through flame of beam of light, rays passing through zone of greatest change of density have the largest angle of refraction. Thus on the screen on the place corresponding to this region, there appears a shadow, corresponding to the image of the zone of the greatest change of density. Rays passing through flame outside of zone of change of density, including those passing through zone of chemical reaction, are not refracted. Results of experiments of Zarembo and Zel'dovich confirm their assumption concerning thermal structure of flame [64].

Investigations of Zarembo and Zel'dovich make it possible to theoretically and experimentally determine depth of penetration of heat into zone of preliminary heating of Bunsen flame, which is clear confirmation of the thermal theory of burning of gases. Thus they established the erroneousness of the assertion of the Dutch scientists, Van de Poll and Westerdijk [65], that in the zone of sharp change of density of the burning gas chemical reaction occurs. Actually chemical reaction occurs beyond the boundaries of the zone of heating -- of the zone of sharp change of density.

Question of detailed investigation of structure of front of flame has practical value. Knowledge of structure of front of flame makes it possible to pose practically important problems, connected with possibility of intensification and completeness of transformation of original combustible mixtures in the steady-state regime of actual furnace mechanisms.

## Section 2. Method of Studying Kinetics of Chemical Reaction in a Flame

Thanks to the achievements of modern theory of normal burning, investigation of propagation of a flame in gas mixtures is a more powerful means of studying kinetic processes of burning at high temperatures, i.e., reactions, taking place with high rates, which still do not lend themselves to investigation by other methods.

Study of the kinetics of a chemical reaction at high temperatures is a problem which is extremely complicated, and it is no accident that the kinetics of gas reactions at temperatures of more than 1200° K have been very little studied.

Barskiy and Zel'dovich [26], during investigation of combustible mixtures of carbon monoxide established basic mechanisms of oxidation of carbon monoxide in flame. Authors established that the reaction has with respect to carbon monoxide the first order, but with respect to oxygen, with content of the latter in the combustible mixture 5% zero order. Order of reaction with respect to catalyzing agent -- water or hydrogen -- is equal to unity for mixtures with surplus of carbon monoxide, and to one half with surplus of oxygen. Chemical reaction rate of burning is impossible to determine by temperature and composition. Kinetic mechanisms are determined on the basis of results of measurement of speed of flame. Measurement of normal speed of flame of homogeneous fuel mixtures with different temperatures of burning makes it possible to determine activation energy.

Values of activation energy are determined by temperature range in which chemical reaction proceeds, and by order of magnitude of volume rate of heat release in zone of maximum chemical reaction rate. Magnitude of rate of heat release presents very definite practical interest, since thus is determined upper limit of intensification of industrial mechanisms depending on rate of reaction.

Thus it is necessary to select conditions of experiment under which temperature of burning at constant composition of given mixture would change. This will be attained by application of method of Sadovnikov -- dilution of fuel mixture by its combustion products. Experimental data of Sadovnikov [41] are presented in Table 7.

Data of this table are graphically represented in Fig. 26.

By investigating dependence of speed of flame on composition of original mixture, it is necessary to distinguish burning at stoichiometric composition and the influence of deficient and excess components in original fuel mixture.

If it is necessary to establish influence of concentration of oxidizer on speed

Table 7. Influence of Combustion Products on Speed of Flame

(a) Добавки продуктов горения %	(b) Топливная смесь %	(c) Скорость пламени см/сек
(d) Смесь (50% CO + 50% воздуха + 2% H <sub>2</sub> O)		
0	100	62
10	90	50
20	80	40
30	70	25
40	60	17
(e) Смесь (30% CO + 70% воздуха + 2% H <sub>2</sub> O)		
0	100	40,5
10	90	32
30	70	13

KEY: (a) Additions of combustion products; (b) Fuel mixture; (c) Speed of flame cm/sec; (d) Mixture (50% CO + 50% air + 2% H<sub>2</sub>O); (e) Mixture 30% CO + 70% air + 2% H<sub>2</sub>O).

of flame, then one should study not mixtures with deficiency of oxidizer, but mixtures in which concentration of combustible component is kept constant and concentration of oxidizer is varied within as wide as possible limits, while maintaining temperature of burning in the investigated series of experiments constant.

Barskiy [26] experimentally showed that speed of flame, and consequently, chemical reaction rate in flame practically does not depend on concentration of oxygen.

In mixtures (50% CO + 10% O<sub>2</sub> + 40% N<sub>2</sub>; 50% CO + 20% O<sub>2</sub> + 30% N<sub>2</sub>) it is impossible to establish influence of concentration of oxygen on rate of chemical reactions, in view of steep climb of temperature with increase of oxygen. Such influence can be determined by comparison of mixtures in which oxygen is not the deficient component (20% CO + 10% O<sub>2</sub> + 70% N<sub>2</sub>; 20% CO + 30% O<sub>2</sub> + 50% N<sub>2</sub>; 20% CO + 80% O<sub>2</sub>).

In this series of experiments, the original quantity of carbon monoxide proceeding into the zone of burning is constant, but concentration of N<sub>2</sub> and O<sub>2</sub> change correspondingly so that the temperature of burning remains constant. In spite of the fact that concentration of oxygen in zone of reaction was changed from 2 to 72%,



speed of flame wash changed only by 1.5 time.

Experiments with fuel mixtures giving identical temperatures of burning and containing different excess quantities of carbon monoxide showed that normal speed is proportional to square root of concentration of carbon monoxide in zone of reaction. This dependence indicates that chemical reactions in flame have the first order with respect to carbon monoxide.

Zel'dovich and Barskiy [26] developed method of replacement of part of excess component of fuel mixture by inert diluent. This method made it possible to study dependence of speed of flame on composition of mixture at constant value of temperature of burning. They investigated combustible mixtures of carbon monoxide with oxygen and nitrogen with different concentrations of the excess component. Authors succeeded in measuring speed of flame for a number of fuel mixtures, in which reactions in flame proceed under identical conditions, which attained by change of concentration of excess component, replacement of part of it by inert gas. Measurement of speed of flame of appropriately selected fuel mixtures makes it possible to study dependence of chemical reaction rate in flame on temperature, pressure and composition of mixture.

From theory of speed of flame it follows that value of normal speed of flame is conditioned by chemical kinetics of process of burning in zone of maximum rate of reaction  $u_m \sim \sqrt{w_{max}}$ .

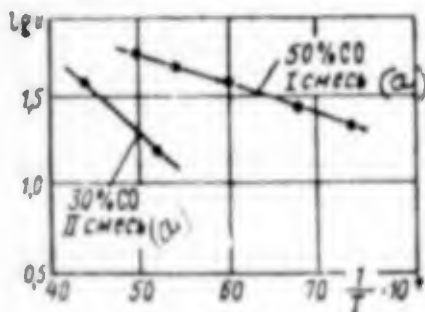


Fig. 26. Influence of combustion products on speed of flame.

$E_{I \text{ mix}} = 25 \text{ Kcal/mole}$ ,  $E_{II \text{ mix}} = 38 \text{ Kcal/mole}$ .

KEY: (a) Mixture;

Since mass rate of burning

$$u_m \sim \sqrt{w_{max}}$$

this dependence can be used for investigation of kinetics of reaction in flame at high temperatures. By variation of parameters of the original mixture, there is presented the possibility of artificially

creating necessary conditions in zone of flame within wide limits. Temperature of



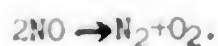
burning can be regulated by change of percentage content of excess component of mixture. At constant concentration of excess component, calorific value of fuel mixture also constant. If we produce partial replacement of excess component of fuel mixture by inert gas of identical heat capacity, then  $T_r$  and  $w_{max}$  will remain constant, but composition will change. By change of speed of burning it is possible to judge concerning kinetics of reaction in flame.

As was discussed above, change of temperature of zone of maximum rate, during conservation of constancy of composition of original fuel mixture, is attained by the method of Sadovnikov. This method can be used to study dependence of rate of reaction in flame on composition of mixture and temperature.

Using method of dilution of fuel mixture with products of combustion, we lower temperature of burning by gradually diluting the mixture (temperature of burning is determined by thermodynamic calculation taking into account the original composition of the mixture). Speed of flame is thus decreased and according to the obtained data one can determine activation energy.

### Section 3. Burning of Mixtures with Oxides of Nitrogen

Mechanisms of burning of mixtures of nitrogen peroxide are intimately connected with study of fuel properties of nitric oxide, whose formation and decomposition can be expected during burning of mixtures of the peroxide according to the scheme:



As can be seen from our investigations, during burning of mixtures of nitrogen peroxide with hydrogen at constant pressure and constant volume, combustion products of first flame contain in large quantity nitric oxide, while combustion in products of the second flame nitric oxide is not observed. Consequently, during burning of mixtures of hydrogen with nitrogen peroxide, it is possible to expect formation, as well as disintegration of nitric oxide under appropriate conditions.

As can be seen from further consideration, nitric oxide has an endothermic nature, but is a thermally stable compound and is subject to disintegration only at high temperatures.

During the study of the influence of additions of nitric oxide to combustible mixtures of hydrogen with nitrogen peroxide, Nasirov and Shaulov discovered the effect of self-retardation by nitric oxide, due to which it is possible to explain the chain character of the mechanism of burning of hydrogen in nitrogen peroxide. This question more specifically will be considered in Section 5.

### 1. Kinetics of Decomposition and Formation of Nitric Oxide

Hinshelwood and his collaborators [66], [67] investigated kinetics of pre-ignition reaction of the technically important mixture of nitric oxide with hydrogen and established that the reaction is homogeneous and proceeds according to the mechanism of termolecular reactions.

Authors consider that during collisions of NO with NO and NO with  $H_2$  there will be formed "complexes" and the reaction occurs in the case when a "complex" will succeed in colliding with one of the active molecules: either with NO, or with  $H_2$ . Under such an assumption, the authors obtain an expression for rate of reaction, according to which the order of the reaction is less than third order and depends on pressure.

Rozlovskiy [68], assuming absolute values of rate of reactions, calculated activation energy under the assumption that the mechanism of reaction is limited to the simplest ternary collisions of  $2NO+H_2$  and that every effective collision leads to transformation of two molecules of NO. Value of activation energy obtained by Rozlovskiy equals 47.8 kilocalories/mole, which coincides well with the value, calculated from the temperature coefficient of chemical reaction rate.

Jellinek [69], investigating kinetics of decomposition of nitric oxide, arrived at the conclusion that the reaction at a temperature of  $1500^\circ C$  is partially

heterogenous; the homogeneous reaction has second order.

Weise and Frech [70], investigating decomposition of nitric oxide in the range of temperatures  $T=872$  to  $1275^{\circ}$  K, showed that the reaction is autocatalytic and is strongly accelerated in the presence of insignificant quantities of oxygen.

Rozlovskiy [68], processing data on the decomposition of nitric oxide, arrived at the conclusion that the reaction is autocatalytic and the influence of oxygen becomes noticeable only at concentrations which are commensurable with concentrations of nitric oxide. Reaction is not complicated by a small quantity of oxygen, and in such a mixture proceeds according to second order.

Zel'dovich, Sadovikov and Frank-Kamenetskiy [71] studied reaction of formation of nitric from the elements and proposed the following chain mechanism:



Authors consider the equilibrium dissociation of oxygen (c) to be the only source of active centers.

Rozlovskiy [72], generalizing data of Weise and Frech [70], Kaufman and Kelso [73], showed that non-branched reaction chains are formed by atomic oxygen and nitrogen. Initial centers appear during dissociation of oxygen on walls of the reaction vessel; then there is established thermodynamic equilibrium. In a wide range of conditions of experiment, decomposition of nitric oxide proceeds in parallel according to chain and bimolecular mechanisms; with moderate contents of oxygen -- mainly according to a bimolecular mechanism. At small concentrations of oxygen it is possible to disregard the influence of the latter.

As Frank-Kamenetskiy [8] indicated, combination of bimolecular and chain mechanisms in one and the same reaction, according to which it is developed in parallel within quite a wide range of change of conditions of experiment, represents a specific peculiarity of composition and formation of nitric oxide. This is

connected as Rozlovskiy showed, with random coincidence of values of preexponential factors and exponents of constants of both rates. Rate constant of chain process characterizes effective value of activation energy ( $E=84.8$  kilocalories/mole), and the bimolecular process -- true value ( $E=78.2$  kilocalories/mole).

## 2. Decomposition of Nitric Oxide in Flame

As can be seen from works of Nasirov and Shaulov [31], [48] in the study of burning of mixtures of nitrogen peroxide with hydrogen in a closed volume, two-phase burning is observed in mixtures with surplus of hydrogen, as well as in mixtures with surplus of oxygen. Decomposition of nitric oxide can be expected in all mixtures with surplus of hydrogen, inasmuch as in the second flame is assumed burning of nitric oxide with hydrogen. Second flame in mixtures with surplus of oxygen, obviously, is connected with thermal decomposition of pure nitric oxide, inasmuch as in products of first flame, presence of hydrogen is not expected. In connection with this, question concerning study of decomposition of nitric oxide in flame during investigations of burning with nitrogen peroxide acquires special importance.

Adams, Parker and Wolfhard [74] in their short report concerning preliminary results of their experiments in the study of decomposition of nitric oxide in flame of Bunsen burner give general conclusions concerning kinetics and the assumed mechanism of reaction in the flame. Authors consider the decisive stage to be bimolecular decomposition of nitric oxide with subsequent fast burning of the thus formed hydrogen-oxygen mixture. As one of the proofs they list the similarity of spectra of flame of decomposition of NO and reaction of  $\text{NO}+\text{H}_2$ .

According to their opinion, preliminary data in the study of dependence of speed of flame on pressure, taking into account shift of equilibrium in products of combustion, indicate bimolecular character of reaction. As can be seen from results of Rozlovskiy, in mixtures which are lean in NO, dependence of  $u_n$  on P may correspond even to the first order of reaction, and at the same time, absolute rates of

reaction in flame can correspond to trimolecular mechanism. Another proof of proposed mechanism is considered to be coincidence of maxima of speed of flame and temperature of burning at stoichiometric composition, at the same time when in mixtures of  $H_2+O_2$  maximum of speed will shift in the direction of surplus of hydrogen.

Preliminary measurements of temperature coefficient of speed of flame, carried out by Wolfherd and his collaborators, indicate that activation energy of reaction in flame is greater than 50 kilocalories/mole.

Authors [74] consider that rate of trimolecular reaction proceeding according to mechanism of Hinshelwood under the conditions of flame, will be less than the rate of bimolecular decomposition. Absence of bands of radical NH in spectrum of flame is considered by authors to be proof of bimolecular mechanism, inasmuch as these bands always appear upon addition of nitrous oxide to burning mixture. However, absence of nitrous oxide in reacting gases still does not indicate impossibility of trimolecular mechanism.

Values of activation energy calculated by Rozlovskiy from temperature coefficient of pre-ignition reaction under the assumption of trimolecular mechanism, from absolute values of its rate and the rate of reaction in flame for mixtures of nitric oxide with hydrogen ( $\alpha = 0.3$ ;  $p_0 = 1$  technical atmosphere), are in good agreement.

The author during comparison of bi- and trimolecular mechanisms for reaction in flame of nitric oxide with hydrogen discovers that speed of flame calculated for first case is five-six times lower than experimental, at the same time when assumption of trimolecular mechanism gives value of speed of 25--30% higher than the true value. Consequently, in flame, rate of trimolecular reaction is higher than that of the bimolecular, and the course of the first should determine the total rate of interaction of nitric oxide with hydrogen.

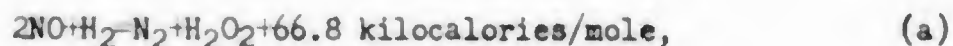
Absolute values of rate of reaction in flame of mixture with weakly dissociated



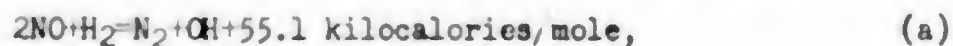
reaction products are in good agreement with those calculated from trimolecular mechanism, at the same time when rate of bimolecular decomposition under these conditions is still insufficient for explanation of observed rates of combustion. In mixtures with strongly dissociated combustion products, rate of reaction in flame is significantly higher than that calculated from trimolecular mechanism, but rate of bimolecular reaction is still less. It follows from this that reaction in flame at high and low temperatures proceeds according to a chain mechanism, and bimolecular decomposition is not realized in flame under any conditions.

### 3. Mechanism of Reaction in Flame of NO+H<sub>2</sub>

Trimolecular mechanism of reaction to a sufficient degree is supported by works of Hinshelwood and his collaborators, but question about reaction products of burning of mixture (NO+H<sub>2</sub>) has remained unexplained. Hinshelwood and Green [66] proposed two variants of the possible mechanism of reaction:



However, it is impossible to exclude the third possible mechanism [83], which includes formation of hydroxyl with subsequent recombination of radicals HNO:



Harteck [75] during interaction of atomic hydrogen with nitric oxide showed formation of HNO.

In the scheme of Taylor and Tenford, radicals of HNO are decomposed without forming reaction chains, which is probably correct for low temperatures. Wolfhard and collaborators exclude presence of radicals of HNO in flame, inasmuch as in this



case is possible reaction  $\text{NO} + \text{HNO} = \text{OH} + \text{N}_2\text{O}$ , which they reject because of absence in flame of  $\text{N}_2\text{O}$ .

Rozlovskiy assumes that radical  $\text{HNO}$ , formed in flame of mixtures with strongly dissociated combustion, products provides possibility of chain mechanism of reaction at high temperatures. Onset of chains occurs by means of diffusion of atomic hydrogen and hydroxyl out of zone of dissociated products of combustion into zone of reaction.

As experiments of Nasirov and Shaulov show [31], in the investigation of influence of additions of nitric oxide to fuel mixture  $\text{NO}_2 + \text{H}_2$ , nitric oxide in flame exhibits inhibitor character -- abruptly decreases speed of flame. Apparently, nitric oxide in flame, due to self-retardation at temperatures of burning  $T_f$  will form radical  $\text{HNO}$ , due to which reaction proceeds according to a chain mechanism.

Indirect confirmation concerning participation of radical  $\text{HNO}$  in chain reaction between nitric oxide and hydrogen is given by Rozlovskiy on the basis of results of Wolfhard and collaborators in the study of burning of mixtures of  $\text{NO}$  with  $\text{NH}_3$ . In spite of lower temperatures of burning these mixtures are more easily ignited and have significantly higher rates.

Authors include in the assumed mechanism the reaction  $\text{NO} + \text{NH} = \text{N}_2 + \text{OH}$ , which is easily realized. Elementary reaction of deoxidation of nitrogen leads to formation of molecule  $\text{N}_2$ , for which reason there is removed the necessity to surmount the energy barrier caused by high energy of dissociation of nitrogen. Therefore one should expect that molecule  $\text{NO}$  will most easily of all interact with radicals containing an atom of nitrogen.

#### 4. Decomposition of Nitrogen Peroxide in Flame

Bodenstein, Ramstetter [76] in their investigation of formation and decomposition of oxides of nitrogen found that reaction of decomposition of nitrogen peroxide  $2\text{NO}_2 = 2\text{NO} + \text{O}_2$  is a homogeneous bimolecular reaction. Norrisch [77] calculated value

of activation energy of bimolecular reaction by theoretical formula  $E = 33.2$  kilocalories and by equation of Arrhenius  $E = 32$  kilocalories.

In the investigation of combustible mixtures of nitrogen peroxide with hydrogen in Bunsen flame Wolfhard and his collaborators arrived at the conclusion that nitrogen peroxide in flame is reduced only to nitric oxide. They find for this additional confirmation in low temperature of burning, measured by them spectroscopically by self-reversal lines of sodium, which is even lower than thermodynamic in such a reaction. Author assumes that decomposition of nitric oxide does not succeed as a reaction between hydrogen and nitrogen peroxide, and in the flame burns only  $H_2+O_2$ .

Our experiments show that constant pressure of burning, reaction products contain nitric oxide and free nitrogen, the ratio of which depends on pressure, as well as on composition of the combustible mixture.

With increase of content of hydrogen in original mixture, quantity of free nitrogen in combustion products is increased, and with increase of nitrogen peroxide -- is decreased. Apparently excess quantity of hydrogen determines formation of free nitrogen in flame.

It is necessary to assume that presence of free nitrogen in combustion products of first flame is connected with interaction of formed nitric oxide in flame, during decomposition of peroxide, with atomic hydrogen in zone of burning. Thus there is formed the radical HNO, which provides the possibility of a chain mechanism of reaction during burning of combustible mixtures of nitrogen peroxide.

#### Section 4. Two-Flame Burning

Investigation of flames with oxides of nitrogen as oxidizers is an important and little-studied area of the theory of burning.

Study of these flames, besides theoretical interest, can have also important practical value. It is sufficient to remember that oxides of nitrogen are decomposition products of explosives. Study of mechanisms of burning of mixtures of

nitrogen peroxide is intimately connected with study of properties of mixtures of nitric oxide, formation of which one should expect during deoxidation of nitrogen peroxide.

In the literature are available data of Adams, Parker and Wolfhard [74] concerning burning of mixtures of nitrogen peroxide with hydrogen in Bunsen flame. Maximum observed normal speed of flame ( $\sim 2.6$  m/sec) corresponds to the ratio  $H_2/NO_2=1$ . In connection with this, the mentioned authors consider that deoxidation of nitrogen peroxide in flame can be only to nitric oxide. This statement is confirmed by low temperature of burning  $T_f$ , measured by them spectroscopically by reversal of line of sodium, which is even lower than thermodynamic in such a reaction.

In 1954 there appeared work of Parker and Wolfhard, in which was determined speed of propagation and temperature of flame in mixture of hydrogen with oxide and nitrogen peroxide.

Pannetier and Sikar studied propagation of flame in mixtures of hydrocarbons and nitrous oxide ( $N_2O$ ). Their curious experiments, showing that region of propagation of flame for mixtures ( $C_4H_{10}+N_2O$ ) and ( $C_4H_{10}+N_2+1/2O_2$ ) are different which excludes the possibility of primary decomposition according to the equation ( $N_2O \rightarrow N_2 + \frac{1}{2}O_2$ ). This confirms conclusion of authors that initial stage of burning of hydrocarbons with nitrous oxide ( $N_2O$ ) is decomposition of molecule  $N_2O$  with formation of nitric oxide. This conclusion is confirmed by presence of bands of NO in spectra of flames of saturated hydrocarbons with nitrous oxide.

Nasirov and Shaulov [31], [48] studied burning of mixtures of nitrogen peroxide with hydrogen and methane by photographing propagation of spherical flame in glass bulb (volume of bulb was  $430 \text{ cm}^3$ ) with central ignition, on revolving film by the usual method at pressures of 250 mm of mercury.

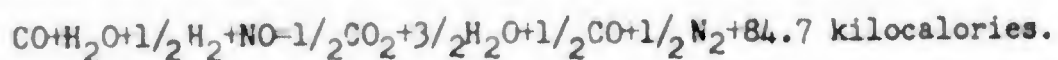
As is known, under these conditions on a large segment of path of flame (to 30--50%) burning remains practically isobaric, and photography gives speed of flame in relation to motionless combustion products  $u_b$ , which can be converted to normal

speed  $u_n$ , if change of densities during combustion  $\mu$  is known.

Photographs of flame obtained by authors reveal an unusual property: on them is shown the consecutive propagation of two flames, divided by intervals of time on the order of several thousandth of a second. In all investigated mixtures containing from 33 to 54%  $\text{NO}_2$ , there was observed consecutive propagation of two flames. Analogous two-flame burning was observed by Nasirov and Shaulov [48] for mixtures of  $\text{NO}_2+1.25 \text{CH}_4$ .

Phenomenon of two-stage burning was known also earlier. It was discovered by Zel'dovich and Shaulov, who burned in spherical vessel the simplest explosive -- vapors of methyl-nitrate ( $\text{CH}_3\text{ONO}_2$ ) in 1946 [47]. On photographic prints was observed an unexpected picture: track of propagation of flame was separated from track of spark on photograph by a completely unlighted interval. Length of interval (along time axis) corresponded to an interval of 0,01 sec between jump of the single spark and beginning of propagation of flame from the center of bulb to periphery (Fig. 27).

Two-stage burning was explained by Zel'dovich and Shaulov by formation of combustible mixtures of nitric oxide as reaction products of "first flame" ( $\text{CH}_3\text{ONO}_2 = \text{CO} + \text{H}_2 + 1/2 \text{H}_2 + \text{NO} + 30.8$  kilocalorie). Inertness of oxide nitric leads to the fact that without an additional stimulator, the reaction is stopped at this stage. Additional factor of appearance of "second flame" is adiabatic compression of gases with corresponding heating, leading to combustion of fuel mixture -- of products of "first flame" with complete deoxidation of nitric oxide according to the reaction



As it is known, in combustion products under these conditions appear significant temperature gradients, caused by adiabatic compression on last stages of combustion of mixture. Thus is possible adiabatic ignition of combustible mixtures of nitric oxide formed after passage of "first flame". Calculations of critical conditions of ignition of mixtures of  $\text{NO} + \text{H}_2$ , carried out by Rozlovskiy, and the works of Adams, Parker and Wolfhard, Masirov and Shaulov confirmed validity of assumption of

Zel'dovich and Shaulov.

Propagation of second flame can be prevented under the conditions when there does not occur adiabatic compression. This was realized during burning of methyl-nitrate in a vessel separated by a thin rubber diaphragm from a buffer volume filled with inert gas.

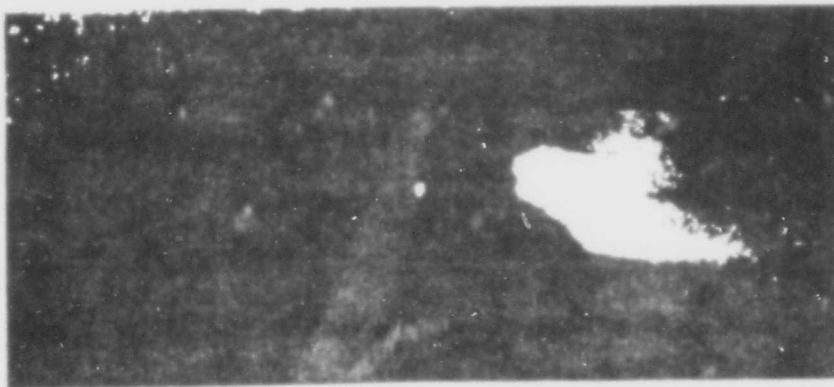


Fig. 27. Photograph of two-flame burning of vapor of methyl-nitrate (Zel'dovich, Shaulov [58]).

During small increase of pressure, diaphragm easily is torn, and in view of the large volume of the buffer vessel, at subsequent stages of burning, pressure remains practically constant.

In this case analysis of reaction products detected formation of large quantities of nitric oxide, which were completely absent during burning in a closed volume.

On the basis of these facts Nasirov and Shaulov advanced the assumption that two-stage burning of mixtures  $H_2+NO_2$  and  $CH_4+NO_2$  is connected with deoxidation of nitrogen peroxide to nitric oxide in the first flame, with subsequent adiabatic ignition of the formed products if incomplete combustion due to the Mach effect. A curious trait of the phenomenon is the possibility of such a mechanism not only during disintegration of a complex molecule of nitroether, which includes a combustible component and an oxidizer, but also during burning with participation of a simple molecule of nitrogen peroxide.

Check of the hypothesis was produced by the same method of localization of reaction on the first stage, which was used in the work of Zel'dovich and



Shaulov [47]. Experiments showed that reaction products in the first flame contain nitric oxide and free nitrogen, the ratio of which depends on pressure and initial composition of combustible mixture. Consequently, there flow two parallel reactions, rates of which depend in different ways on conditions of experiment (composition and pressure). By special check was proven completeness of combustion and absence of nitrogen peroxide in reaction products of first flame. At the same time, during burning in closed volume, nitric oxide in practice in products of reaction is not contained.

In Fig. 28 and 29 is presented dependence of fraction of nitrogen from the peroxide  $x = \text{NO}/(\text{NO} + 2\text{N}_2)$  pressures  $p$  and excess oxidant ratio  $\alpha$  (calculated taking into consideration reaction  $\text{NO}_2 + 2\text{H}_2 = 1/2 \text{N}_2 + 2\text{H}_2\text{O}$ ).

As can be seen from the drawings the quantity  $x$  is decreased with increase of pressure and with increase of content of nitrogen peroxide in the original mixture.

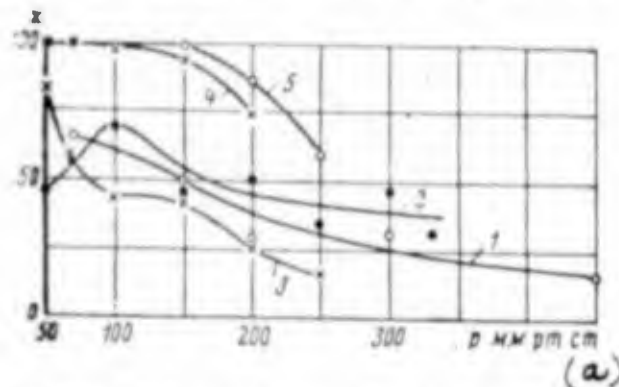


Fig. 28. Dependence of fraction of nitrogen from nitrogen peroxide remaining combined  $x$  on pressure  $p$ .  
 1--  $\alpha = 1.0$ , 2--1.2, 3--1.4, 4--1.54, 5--1.83  
 KEY: (a) mm Hg.

Burning of mixtures with  $\alpha > 1.5$  at  $p < 150$  mm of mercury proceeds practically up to nitric oxide. During burning of a mixture with  $\alpha = 1.0$  at  $p = 450$  mm of mercury, altogether 16% of combined nitrogen remain unreduced and in a mixture with  $\alpha = 1.4$  at 250 mm of mercury -- 17.5%.

Experiments with localization of burning, on the first stage show that nitrogen peroxide reacts with hydrogen according to a complex mechanism which is not included within the scope of concepts of Adams, Parker and Wolfhard, inasmuch as under



definite conditions there can completely be reduced significant quantities of combined nitrogen. Another fact witnessing the complexity of the mechanism of reactions is the position of maximum on the curve  $u_n$  (Fig. 30). As it is known, maximum of speed of flame usually lies near stoichiometric composition. Accordingly this position of maximum in works of mentioned authors will be attained at  $\alpha = 2.0$ . In our experiments  $u_n$  has a maximum at  $\alpha = 1.58$  [48].

Calculation of composition of combustion products in the first flame according to data of chemical analysis under the assumption of absence of dissociation, and determination by energy balance of temperature of burning give a value of  $T_r$  from  $1970^\circ$  to  $2360^\circ$  K, which contradicts data of measurements of English authors [74]. For such temperatures the assumption concerning absence of dissociation becomes groundless, and the possibility of a thermodynamically non-equilibrium state in combustion products, moreover, in the presence of large quantities of radicals is doubtful. One should also consider that at such temperatures critical pressures of ignition of mixtures of NO do not exceed several tens of millimeters of mercury.

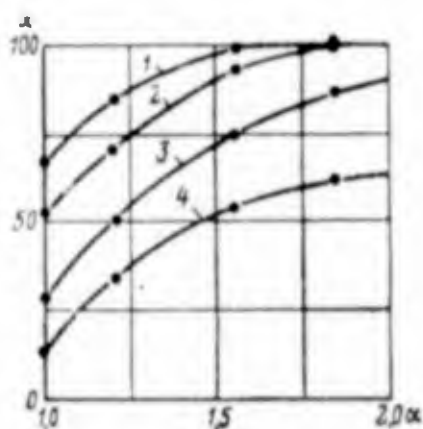


Fig. 29. Dependence of fraction of nitrogen from nitrogen peroxide remaining combined.

$x$  from excess oxidant ratio  $\alpha$ . 1-- $P=100$  mm of mercury, 2-- $150$  mm, 3-- $200$  mm, 4-- $250$  mm.

Study of principles during burning of mixtures of hydrogen with nitrogen peroxide shows that parameter  $NO/N_2$  determines completeness of deoxidation of nitrogen peroxide. This parameter can also characterize burning of fuel systems containing nitric acid and oxides of nitrogen as oxidizers, apparently leading to formation of burning in subsequent stage of nitric oxide. It is known that nitric acid at a temperature of  $550^\circ\text{C}$  is decomposed according to the reaction  $HNO_3 = NO_2 + OH$ , and in the future nitrogen peroxide reacts with hydrocarbons, with formation of nitric oxide and

intermediate products with low stability, which are reduced on the last stage of

burning. On the basis of works of Zel'dovich and Shaulov [47], Nasirov and Shaulov [48], it is possible to affirm that systems containing  $\text{NO}_2$  as one of components ( $\text{NO}_2+\text{H}_2$ ,  $\text{NO}_2+\text{CH}_4$ ,  $\text{NO}_2+\text{C}_6\text{H}_6$ , etc.), and also organic molecules containing the group  $\text{NO}_2(\text{CH}_3\text{ONO}_2$ , et al.), burn in stages, and deoxidation of nitrogen occurs according to the scheme  $\text{NO}_2 \rightarrow \text{NO} \rightarrow \text{N}_2$ .

The reaction of reduction of nitrogen has a large practical value, since this reaction determines burning of solid substances containing  $\text{NO}_2$ .

On the basis of study of mechanisms of burning of mixtures containing nitrogen peroxide at different pressures, there can be made the conclusion that ratio of concentration of intermediate product (NO) during combustion of combustible mixtures containing  $\text{NO}_2$  to concentration of product of complete reduction of nitrogen ( $\text{N}_2$ ) --  $\text{NO}/\text{N}_2$  is a parameter which determines completeness of transformation of mixture with oxidizer  $\text{NO}_2$ . Rocket fuels on the basis of oxidizer -- nitric acid contain free  $\text{NO}_2$ , and nitric acid itself at a temperature of  $650^\circ\text{C}$  is decomposed according to reaction  $\text{HNO}_3 \rightarrow \text{NO}_2 + \text{H}_2\text{O}$ ; and in its turn  $\text{NO}_2$ , reacting with hydrocarbons, will form nitric oxide and unstable intermediate products, reduced in the last stage of burning. This circumstance gives grounds to affirm that parameter  $\text{NO}/\text{N}_2$  can serve for determination of limits of speeding up of motors operating on nitric-acid fuel with respect to pressure [47], [48], [182].

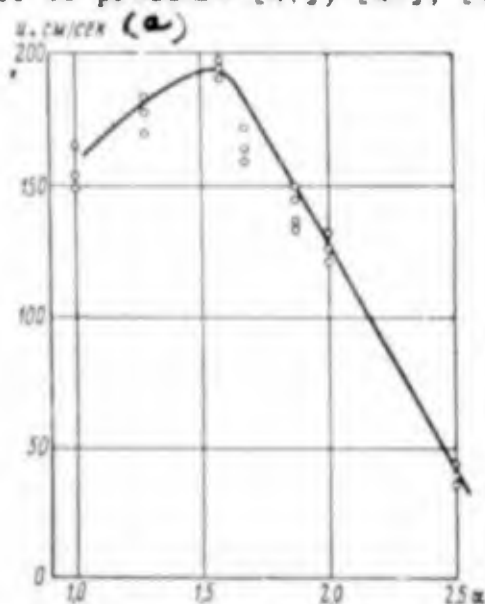


Fig. 30. Dependence of normal speed of flame on composition of mixture ( $\text{NO}_2+\text{H}_2$ ) at  $P=200$  mm of mercury.

KEY: (a) cm/sec.

## 1. Critical Conditions of Ignition of Mixtures of Nitric Oxide

Interaction of nitric oxide with hydrogen in the region of moderate temperatures proceeds according to a trimolecular mechanism. Rozlovskiy, using the method of Frank-Kamenetskiy predicted possibility of self-ignition of these mixtures and calculated critical conditions of ignition.

Calculation has been performed for conditions of experiments of Hinshelwood and his collaborators, which were conducted in a spherical vessel with a volume of  $300 \text{ cm}^3$  for a mixture with  $\alpha=0.667$ . Activation energy is taken equal to 47.8 kilocalories/mole. Since temperature of experiments of Hinshelwood did not exceed  $1100^\circ \text{ K}$  and pressure did not exceed 600 mm of mercury, authors did not detect self-ignition of mixtures of nitric oxide with hydrogen.

Results of calculations of critical conditions of ignition are presented in Fig. 31.

Rozlovskiy compared results of his calculation with experimental data of Zel'dovich and Shaulov concerning burning of vapor of Methyl-Nitrate ( $\text{CH}_3\text{ONO}_2$ ). Products of burning of vapor of Methyl-Nitrate at constant pressure consisted approximately of 70% nitrogen in the form of NO, while burning in a closed vessel lead to complete reduction of combined nitrogen. Reaction proceeded in two stages with consecutive propagation of two flames.

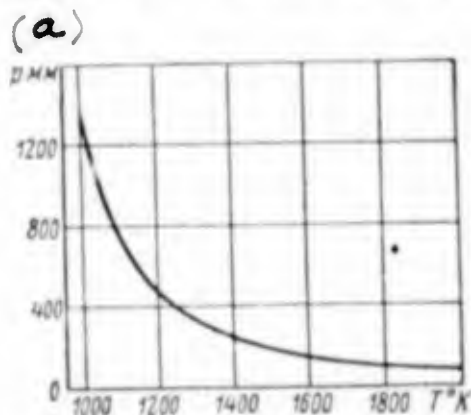


Fig. 31. Critical conditions of ignition of mixture  $\text{NO}+\text{H}_2$  (Rozlovskiy).  
KEY: (a) mm.

Products of reaction of first flame are heated due to adiabatic compression, leading to appearance of temperature gradient. Then products of first flame ( $\text{CO}+\text{H}_2\text{O} \text{ NO}+1/2 \text{ H}_2$ ) are ignited in center of vessel with propagation of second flame, which leads to complete reduction of combined nitrogen.

Removal of adiabatic compression of products of first flame eliminated appearance of

second flame. As Zel'dovich and Shaulov showed [47], in the first flame of Methyl-Nitrate there is developed temperature  $\sim 1300^\circ \text{K}$ . From Fig. 28 it follows that at initial pressure of experiment of 500 mm of mercury, self-ignition of mixtures of nitric oxide still is impossible. Toward the end of propagation of first flame, pressure grows by 20 times, as a result of adiabatic compression, temperature in center of vessel reaches  $2500^\circ \text{K}$ .

Critical pressure of ignition of products of first flame, according to Rozlovskiy, should constitute 70--100 mm.

## 2. Effect of Self-retardation of Reaction in Flame

In the given paragraph is considered self-retardation action of nitric oxide on speed of flame in the front of the flame. Nitric oxide is one of the components of combustion products during burning of mixture of hydrogen with nitrogen peroxide, and is an inhibitor, decelerating chemical reaction in the flame. Semenov [78] showed that nitric oxide in many valuable reactions is known as a strong retardant, terminating chains.

As experimental investigations of Nasirov and Shaulov show [31], nitric oxide is an inhibitor of chemical reaction in the front of the flame. The inhibiting character of nitric oxide was established by measurement of speed of flame during corresponding introduction of different concentrations of nitric oxide into the combustible mixture of nitrogen peroxide with hydrogen. This effect was confirmed by sharp change of speed of flame upon addition of NO and by different values of activation energy upon dilution of fuel mixture by nitric and nitrogen.

During the study of dependence of speed of propagation of flame on original composition in fuel mixtures of nitrogen peroxide with hydrogen, it was established that maximum of speed of flame corresponds to mixtures with  $\alpha \sim 0.79$ , i.e., mixtures, rich in fuel.

Displacement of maximum of speed in the direction of mixtures rich in fuel

is explained by the effect of self-retardation of nitric oxide in flame; formed nitric oxide in flame interacts with atomic hydrogen and weakens the mixture. It

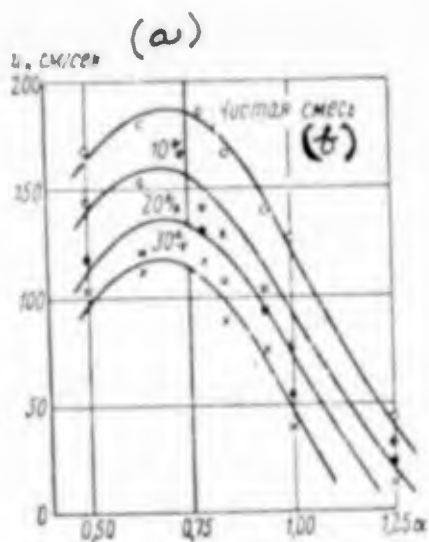


Fig. 32. Influence of additions of  $N_2$  on speed of flame of mixture ( $NO_2+H_2$ ) (Nasirov, Shaulov).  
KEY: (a) cm/sec; (b) pure mixture.

is necessary to note that this assumption gives the rights to consider that during burning of nitrogen peroxide with hydrogen, the reaction proceeds according to chain mechanism. Only in the presence of a chain mechanism could nitric oxide, as an addition and as a product of reaction, effect the rate of reaction as an automatic inhibitor.

Abundance of nitric oxide in flame of mixtures rich in nitrogen peroxide leads to sharp lowering of speed of flame (Fig. 32). Further, during burning of  $NO_2+H_2$ , in products of flame along with nitric oxide is detected also molecular nitrogen. Thus the quantity of free nitrogen in products of reaction with increase of fuel in mixture is increased, but with increase of nitrogen peroxide -- is decreased.

The authors are inclined to consider that formation of free nitrogen is connected with the effect of autoinhibition in flame, i.e., with interaction of nitric oxide with atomic hydrogen there is formed an intermediate compound  $HNO$ . Apparently, large concentration of nitric oxide in reaction products weakens action of autoinhibition, and formation of nitrogen practically does not take place.

On the basis of what has been stated above, Nasirov and Shaulov arrived at the conclusion that during burning of nitrogen peroxide with hydrogen, in flame occurs/ self-retardation -- autoinhibition of the chemical reaction, forming in the first stage of burning nitric oxide in the zone of burning.

In mixtures of nitrogen peroxide with methane, Nasirov and Shaulov studied influence of temperature of burning /on normal speed of flame. Change of temperature of burning



in flame was realized by method of dilution of fuel mixture with its combustion products — nitric oxide and molecular nitrogen, which was used also during investigation of combustible mixture of nitrogen peroxide with hydrogen.

For study of influence of additions on speed of flame in fuel mixtures of nitrogen peroxide with methane speed of flame was measured at different concentrations of diluent and original mixture. All experiments were performed at initial pressures  $p_0 = 200$  mm of mercury.

In Fig. 33 are shown curves representing the influence of additions of nitrogen and nitric oxide to combustible mixtures of nitrogen peroxide with methane on speed of flame for different compositions ( $\alpha = 1.3, 1.8$  and  $3.0$ ) mixtures.

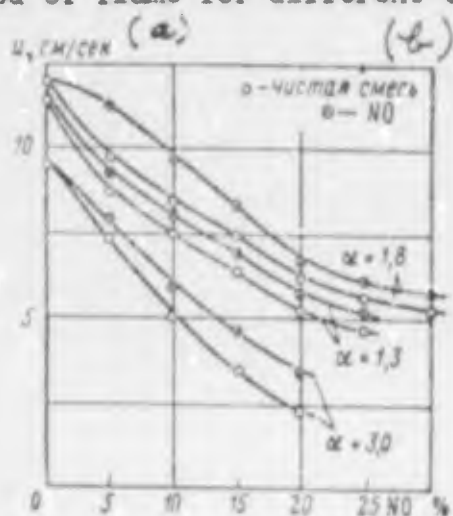


Fig. 33. Influence of additions of nitric oxide on speed of flame of mixture  $\text{NO}_2 + \text{CH}_4$  at  $p = 200$  mm of mercury (Nasirov, Shaulov).  
KEY: (a) cm/sec; (b) Pure mixture.

As can be seen from Fig. 34, with increase of percentage content of addition of nitrogen and nitric oxide in original mixture, speed of flame is decreased. As experiments show, decelerations of flame with increase of concentration of additions of nitrogen and nitric oxide in original mixture are practically identical.

Consequently, nitric oxide is the same kind of inert diluent, as molecular nitrogen, i.e., nitric in fuel mixtures of nitrogen peroxide

with methane does not exhibit the inhibitor character which was observed in mixtures of nitrogen peroxide with hydrogen. It is probable that here does not take place the effect of autoinhibition by nitric oxide in the flame.

During calculation of value of effective activation energy of chemical reaction was used the known dependence  $u_n \sim e^{-E/2RT}$ . Value of activation energy  $E$  was found from value of angle of slope of straight line in coordinates  $\ln u_n - (1/T_r)$ .



Calculated value of activation energy of chemical reaction for mixtures of nitrogen peroxide with methane equals  $E=15.5$  kilocalories/mole. Values of activation energy calculated upon dilution of mixtures with nitrogen and nitric oxide agree well.

In the literature there are also other examples of the retarding action of nitric oxide, for example McDowell and Thomas [79] during investigation of low-temperature thermal oxidation of acetaldehyde in the gaseous phase detected retarding action of impurity of nitric oxide. An insignificant quantity of nitric oxide abruptly decreased chemical reaction rate.

Investigations were carried out by the photoelectric method. Authors measured rate of disappearance of nitrogen peroxide in time, mainly in the interval of time corresponding to the period of induction  $\tau$ . Further, based on the assumption that a large part or all of the inhibitor is expended during the time of the period of induction  $\tau$ , they determined rate of deceleration of reaction  $w_T$  by the equation

$$w_T = \frac{C_{NO_2}}{\tau}, \quad (3.12)$$

where  $C_{NO_2}$  -- initial concentration of nitrogen peroxide.

Authors established that rate of disappearance of nitrogen peroxide proceeds according to first order. Rates of expenditure of nitrogen peroxide are identical during the period of induction and after. Activation energy of reaction of expenditure of nitrogen peroxide calculated by the authors is equal to 16.8 kilocalories/mole.

As experiments show, nitrogen peroxide reacts with acetaldehyde quantitatively, forming thus nitric oxide. On the basis of analyses of experimental data, McDowell and Thomas come to the conclusion that deceleration of oxidation of acetaldehyde apparently is caused by the presence of nitric oxide combined with the acetyl radical, which, as a rule, is the initiator of the oxidizing chain. Only such an assumption leads the authors to a good explanation of experimental results.

Wolfhard and his collaborators explain the inhibiting character of NO by the unpaired electronic structure of this molecule. During collisions with free radicals of chains it is joined to them easily at moderate temperature.\* However, as experiments of Nasirov and Shavlov show, nitric oxide exhibits an inhibitor character also at temperatures of burning  $T_r$ .

During investigation of combustible mixtures of nitrogen peroxide with hydrogen, in the study of effect of different additions to fuel mixture, it was discovered that nitric oxide as an addition to the combustible mixture exhibits an inhibitor character -- decelerates the reaction in the flame.

Study of influence of the inhibitor, oxide of nitrogen, on speed of flame during burning of nitrogen peroxide with hydrogen was carried out in closed volume by means of measurement of speed of propagation of flame at different percentage contents of inhibitor. As experiments show, upon addition of nitric oxide to fuel mixture  $\text{NO}_2 + \text{H}_2$  speed of flame is decreased and beyond a certain percentage content of NO, the mixture is not at all ignited. Experiments were carried out at constant initial pressure of fuel mixture for different compositions  $\alpha = 1.0$  to 2.5 (see Table 8).

As can be seen from Table 8, at one and the same percentage content of additions of nitrogen and nitric oxide, temperature of burning differs insignificantly -- by  $4^\circ$ -- $12^\circ\text{C}$ , which it is possible to consider practically constant.

Speed of flame after dilution of fuel mixture by nitric oxide falls almost by 4--5 times more than after dilution by nitrogen, at one and the same percentage content of both diluents -- impurities (Fig. 33). This shows that deceleration of propagation of flame upon addition of nitric oxide is connected not with decrease of temperature, but only with concentration of nitric oxide in original

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\* Nitric oxide can act as an accelerator at high temperatures, reacting with molecules of original substances and creating thus new free radicals. (Ed. Note).

Table 8. Effect of Additions on Speed of Propagation of Flame in Mixtures  $\text{NO}_2+\text{H}_2$ . (According to data of Nasirov and Shaulov).

		Чистая смесь	(b) Добавка $\text{N}_2$ в %						
			5	10	15	20	25	30	35
$\alpha=1.0$	$\frac{u_n}{T^\circ \text{K}}$ (a)	158 1912	156 1892	144 1865	130 1845	118 1820	110 1792	104 1764	102 1728
$\alpha=1.28$	$\frac{u_n}{T^\circ \text{K}}$ (c)	180 2110	164 2085	152 2052	135 2024	120 1984	116 1952	112 1912	100 1876
$\alpha=1.58$	$\frac{u_n}{T^\circ \text{K}}$ (c)	186 2260	144 2238	140 2196	134 2172	132 2130	120 2084	118 —	110 1984
$\alpha=1.68$	$\frac{u_n}{T^\circ \text{K}}$ (c)	165 2324	144 —	130 2254	114 2208	108 2170	100 2132	90 2082	84 2032
$\alpha=1.88$	$\frac{u_n}{T^\circ \text{K}}$ (c)	137 2424	114 2370	104 2310	98 2285	94 2245	86 2204	78 2145	— —
$\alpha=2.0$	$\frac{u_n}{T^\circ \text{K}}$ (a)	128 1460	75 2398	65 2355	54 2312	50 2268	44 2228	37 2156	30 2100
$\alpha=2.5$	$\frac{u_n}{T^\circ \text{K}}$ (c)	43 2008	35 1968	32 1932	29 1900	28 1864	24 1820	20 1776	28 1732

		Чистая смесь	(b) Добавка $\text{NO}$ в %						
			5	10	15	20	25	30	35
$\alpha=1.0$	$\frac{u_n}{T^\circ \text{K}}$ (c)	168 1912	112 1892	84 1860	58 1940	44 1916	35 1784	24 1756	— —
$\alpha=1.28$	$\frac{u_n}{T^\circ \text{K}}$ (c)	180 2110	146 2096	124 2060	110 2022	91 1984	84 1972	76 1912	60 1876
$\alpha=1.58$	$\frac{u_n}{T^\circ \text{K}}$ (c)	186 2260	124 2223	108 2200	100 2168	94 2120	86 2076	70 2020	64 —
$\alpha=1.68$	$\frac{u_n}{T^\circ \text{K}}$ (c)	165 2324	40 2296	26 2260	16 —	10 2168	— —	— —	— —
$\alpha=1.88$	$\frac{u_n}{T^\circ \text{K}}$ (c)	137 2424	82 2364	64 2332	54 —	50 2240	48 2196	43 2144	40 2096
$\alpha=2.0$	$\frac{u_n}{T^\circ \text{K}}$ (c)	128 2460	60 2316	51 —	43 —	40 —	35 2210	32 2140	28 2088
$\alpha=2.5$	$\frac{u_n}{T^\circ \text{K}}$ (c)	43 2008	28 1940	24 1918	20 1892	17 1848	15 1804	12 1764	10 1732

KEY: (a) Pure mixture; (b) Addition in %; (c) cm/sec.

mixture, i.e., with increase of concentration of nitric oxide chemical reaction rate in flame is decreased. This fact gives the right to consider action of nitric oxide to be negatively catalytical, decelerating the reaction.

By measuring speed of propagation of flame in fuel mixtures of nitrogen

peroxide at different percentage contents of nitric oxide in original mixture, change of speed of flame depending upon concentration of NO, the inhibitor was established.

We will determine the activation energy of the chemical reaction during participation in the mixture of nitric oxide from the graph of  $\lg u_{NO} - (1/T_r)$ . Value of activation energy thus equals  $E=33$  kilocalories/mole, which differs from value of activation energy calculated for case of dilution of fuel mixture  $NO_2+H_2$  with nitrogen, which is inert by 10 kilocalories/mole. Difference in values of activation energy  $\Delta E=10$  kilocalories/mole also serves as confirmation of inhibiting action of nitric oxide in flame.

Order of reaction with respect to the inhibitor is determined in the following manner: We will designate speed of flame with dilution of original combustible mixture (nitrogen peroxide with hydrogen) by nitric oxide (inhibitor) by  $u_{NO}$ , and with dilution by pure nitrogen (inert) by  $u_{N_2}$ . If ratio of speeds of flame with identical percentage contents of nitrogen and nitric oxide in original mixture is designated by  $\pi = u_{NO}/u_{N_2}$ , then order of chemical reaction with respect to inhibitor will be

$$n = \frac{d \ln \pi}{d \lg (\%NO)} \quad (3.13)$$

where % NO shows at what percent of NO in the mixture is taken the ratio of speeds of flame.

In Fig. 34 is shown dependence of change of speed of flame on percentage content of nitric oxide at different compositions of the combustible mixture  $NO_2 + H_2$ .

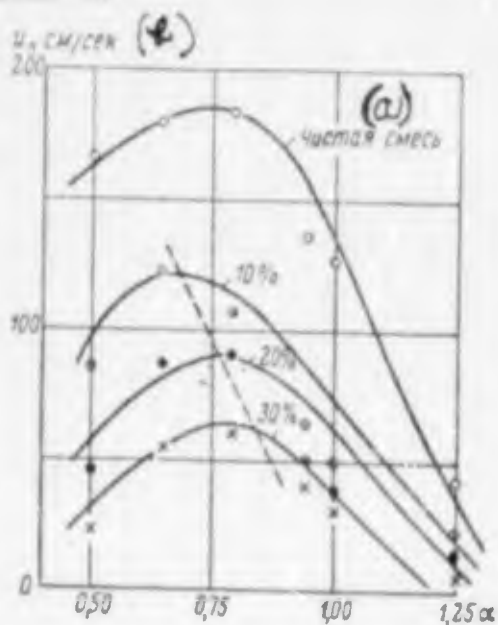


Fig. 34. Dependence of normal speed of flame on percentage content of nitric oxide in mixture ( $NO_2+H_2$ ) at different compositions (Nasirov, Shaulov). KEY: (a) Pure mixture; (b) cm/sec.

## CHAPTER IV

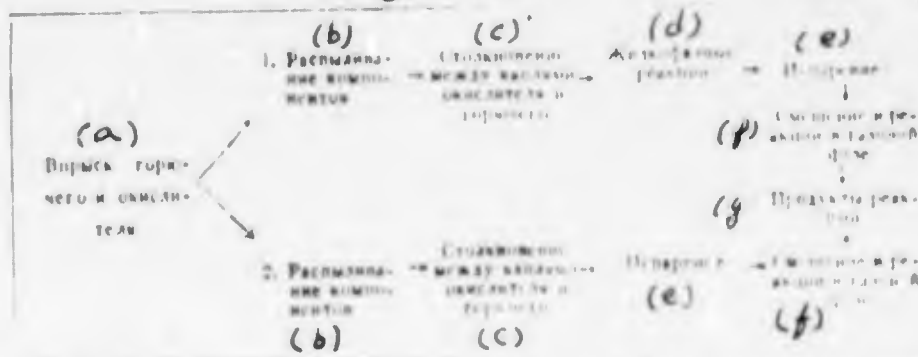
### CARBURETION

One of the urgent problems in the area of design of motors is the search for methods of control of carburetion and combustion of fuel in combustion chamber. Solution of this problem is quite difficult.

Process of carburetion, depending upon nature of fuel components, can proceed in two directions.

The first diagram describes carburetion of spontaneously inflammable fuels, and the second — carburetion of non-spontaneously combustible fuels. These diagrams significantly are complicated by the appearance in the chamber of vortical motion. Vortical motion is accompanied by counter-currents from zone of burning into zone of mixing and promotes best mixing of fuel and oxidizer, and consequently increases completeness of transformation of fuel mixture into combustion products.

Diagram [182]



KEY: (a) Injection of fuel and oxidizer; (b) Atomization of components; (c) Collision between drops of oxidizer and fuel; (d) Liquid-phase reactions; (e) Evaporation; (f) Mixing and reactions in gas phase; (g) Reaction products.

Carrying out analysis of operating process, taking into account vortical motion and counter-currents requires special consideration. In this chapter are considered atomization, evaporation, mixing and delay of ignition of fuel systems.

Processes of liquid-phase oxidation which are peculiar to spontaneously igniting fuels, proceed mainly during emergence of the motor into its regime and are not discussed by us.

### Section 1. Atomization of Fuel

Problems connected with formation of atomized fuel of definite structure in the combustion chamber caused the appearance of a large number of works, which before the 1940's concerned mainly motors with ignition due to compression.

The rapid development of the air-breathing jet engine and liquid-fuel rocket engine gave these problems new directions and again underlined the urgency of study of the process of atomization of fuel. Emergence of the liquid-fuel rocket engine into a steady-state regime, its power and economic indices, and also stability of the entire operating process to a significant degree depend on the character of distribution of fuel in the combustion chamber. The entire complex of phenomena connected with atomization of fuel can be divided into two processes: phenomena occurring in the fuel supply system, and phenomena occurring in the combustion chamber.

In the first process are combined all those phenomena which take place in the pipe lines and in the injector nozzles, and in the second — phenomena connected with breaking up of the jet and formation of the drop mixture.

Length of pipe lines and their cross sections, structural arrangement of injector nozzles, state of the medium where injection is produced, physical properties of fuel determine initial parameters of process of atomization.

Range of jet, angle of spray, distribution of drops in volume and their diameters are parameters which characterize the final stage of atomization. In the



future account are considered questions of atomization having important value for carburetion and combustion of fuel.

### 1. Movement of Liquid in Fuel Supply System

Analysis of oscillograms of movement of liquid in system of fuel supply shows that very frequently there appear sharp oscillations of pressure at ends of pipe lines near injector nozzles. These oscillation are propagated with speed of sound along pipe lines and abruptly distort conditions of injection of fuel into combustion chamber.

Theoretical investigation of process of injection, taking into account oscillation of pressure and speed, was carried out in a number of works [80], [82]—[85].

Appearance of oscillations in a system, for example under the conditions of starting of the motor can be represented in the following way.

Fuel or oxidizer moving along pipe lines from tank to head of motor displaces air from system, but due to its low density, outflow of air out of injector nozzle will be observed at a pressure drop which is significantly smaller than that which occurs during outflow of liquid with the same speed. At moment when column of liquid completely displaces air out of pipe line, through nozzle will begin outflow of liquid, and its momentum abruptly will be decreased. Sharp change of condition of moving liquid in system causes appearance of disturbances which strongly distort conditions of atomization of fuel.

Initial equations for analysis of process of injection in the described case are the differential equations of unsteady motion of liquid:

$$\frac{\partial v}{\partial t} = -\frac{1}{\rho} \frac{\partial p}{\partial x} \text{ and } \frac{\partial v}{\partial x} = -\frac{1}{\rho a^2} \frac{\partial p}{\partial t}. \quad (4.1)$$

Simultaneous solution of equations of motion of unsteady flow with boundary conditions is determined by magnitudes of pressure waves and speeds of flow at the beginning of the pipe line and near the head of the motor, and consequently it allows us to determine initial parameters of injection of fuel into combustion chamber [81].

In certain ranges of operation of motor during atomization of fuel, also design of injector nozzles, magnitude of pressure drops across injector nozzles, diameter of nozzle, magnitude of cone of spray [82] have an effect.

## 2. Mechanism of Formation of Drops

Breaking up of jet of fuel occurs under influence of resistance of medium into which fuel is injected, and also under the influence of initial disturbances appearing in the jet during outflow.

External forces which tend to disrupt the jet are counteracted by internal forces of the stream itself. Here are included in the first place surface tension of fuel and internal cohesion of particles.

Disintegration of stream can be divided into four stages (see Table 9).

Table 9. Disintegration of Jet of Liquid.

№ по (a) пор.	Вид распада (b)	Описание процесса (c)
1	(d) Каплевобразование	(h) Жидкость образует капли без струи
2	(e) Распад на капли при вращательно-симметричных колебаниях	(i) Начальные возмущения в сопле приводят к распаду струи на капли. Аэродинамические силы увеличивают амплитуды колебаний
3	(f) Распад при винтосимметричных колебаниях	(j) Струя испытывает волнообразные колебания, приводящие ее к распаду
4	(g) Распыливание	(k) Жидкость, выходящая из сопла с большой скоростью, распадается

KEY: (a) No. in order; (b) Type of disintegration; (c) Description of process; (d) Drop formation; (e) Disintegration into drops during rotationally symmetric oscillations; (f) Disintegration during helically symmetric oscillations; (g) Atomization; (h) Liquid forms drops without a jet; (i) Initial disturbances in the nozzle lead to disintegration of jet into drops. Aerodynamic forces increase amplitudes of oscillations; (j) Jet experiences wave-like oscillations, leading to its disintegration; (k) Liquid leaving the nozzle with high velocity disintegrates.

The first stage corresponds to case of motion of jet with small speeds, when resistance of medium can be disregarded.

Further increase of speed of jet evokes resistance of medium and on its surface in the beginning there appear wave-like disturbances; then they are amplified and the jet of liquid breaks up into part near the exit aperture of the nozzle. Time of disintegration of jet and degree of atomization to a great extent depend on speed of jet. In Fig. 35 are represented speeds corresponding to boundaries of characteristic forms of disintegration of jet depending upon pressure of medium.

Process of development of jet can be represented in the following way. Moving jet comes in contact with medium or in the case of chambers with several injection nozzles, also with neighboring jets and is destroyed — is divided up into parts with different shape and size. Large parts of jet continue to be destroyed further, but small parts of jet, due to action of surface tension assume the form of spheres and form drops. This drop mixture is decelerated by the medium and represents the final product of the process atomization (Fig. 36).

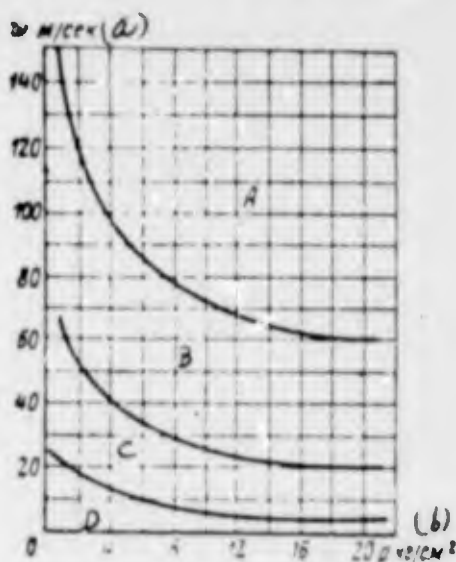


Fig. 35. Dependence of velocity of outflow on pressure of medium. A — region of atomization, B — region of formation of wave-like profile with separation, C — region of formation of wave-like profile, D — region of disintegration [80]. KEY: (a) m/sec; (b) kg/cm<sup>2</sup>.



Fig. 36. Form of disintegration of jet. KEY: (a) Direction of jet.

Theoretical justification for appearance during disintegration of a jet of drops of different diameters was carried out in work [86] on the basis of consideration of unstable capillary waves on the surface of division between two viscous liquids. This problem was solved under the assumption that length of capillary

waves on surface of jet was small compared to radius of jet; consequently, it is possible to carry out analysis of stability of interface between two liquids under action of viscous forces and forces of surface tension by method of small perturbation. These investigations showed that there exists a number of unstable capillary waves, leading to separation from interface of "filaments" of different dimensions, which in the limiting form break up into drops of different dimensions.

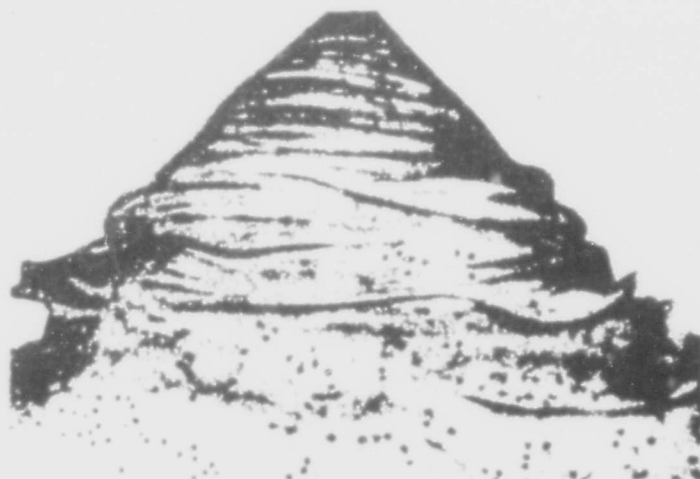


Fig. 37. Photograph of jet of fuel, atomized by centrifugal injector.

Mechanism of formation of drops during outflow from centrifugal injector occurs as a result of disintegration of liquid sheet under the action of the same causes which exist in case of a jet (Fig. 37, 38).

Centrifugal injector is one of the most simple mechanisms employed for atomization of liquid. It consists of a "swirl" chamber with tangential entrance apertures and centrally located nozzle. Liquid is introduced into the chamber through tangential entrance apertures and flows out through nozzle. Due to tangential location of inlet channel, a stream of liquid at the inlet into the internal chamber of the injector is twisted and, moving in a spiral, flows through the nozzle.

Liquid, moving inside the injector along some helical line, will form in it a "vortex", i.e., a cylindrical cavity, the internal part of which is free of liquid.

Outflow of liquid occurs in the form of an undisintegrated sheet with conical surface near the nozzle. The film, due to forces of surface tension, does not break up immediately on exit from the injector but forms, as it were, an elastic "tube" which rapidly disintegrates into small drops.

Operation of centrifugal injector for the first time was investigated by Abramovich [87], [88]. He gave formulas for calculation of coefficient of discharge  $\mu$  and for selection of design parameters of injector.

Coefficient  $\mu$  in the equation of discharge

$$Q = \mu \pi r_c^2 \sqrt{2g\Delta p} \quad (4.2)$$

for an injector with radius of nozzle  $r_c$ , equals

$$\mu = \frac{1}{\sqrt{\frac{1}{\varphi^2} + \frac{A^2}{1-\varphi}}} \quad (4.3)$$

where  $\varphi$  and  $A$  are dimensionless parameters depending on design of injector (Fig. 39) and connected by the expression

$$A = \frac{R_{ax} r_c}{\pi r_{ax}^2} \frac{1-\varphi}{\sqrt{\varphi^{3/4}}} \quad (4.4)$$

where  $R_{ax}$  -- distance from axis of injector to axis of tangential aperture;

$r_c$  -- radius of nozzle;

$r_{ax}$  -- radius of inlet aperture;

$\pi$  -- number of tangential apertures.

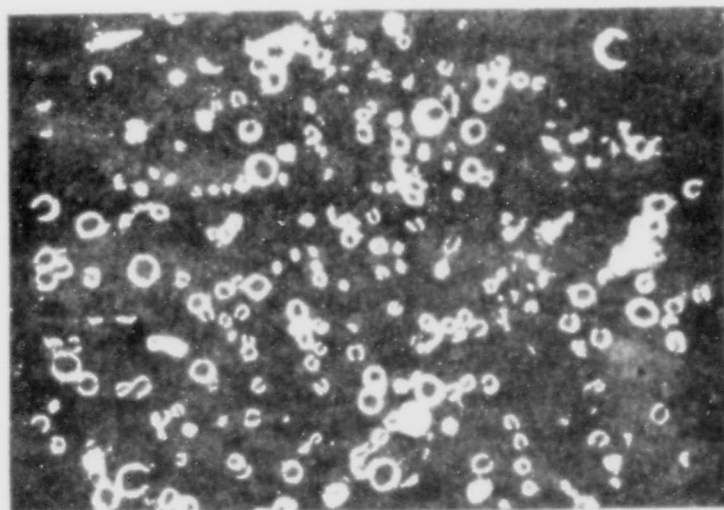


Fig. 38. Typical distribution of drops in jet.

Angle of spray, i.e., angle at vortex of the spray from the injector

$$\tan \frac{\theta}{2} = \frac{1-\eta}{\sqrt{\eta \cdot 2}} \quad (4.5)$$

Form of the jet flowing out of the centrifugal injector depends on velocity of the flowing liquid (Fig. 40). As can be seen from Fig. 40, the greater the pressure drop across the injector, the nearer to the nozzle occurs disintegration of the sheet into drops. In the case of small pressure drop across the injector, the jet is contracted into a bubble (see Fig. 40,a); with increase of pressure drop, the length of the undisintegrated part of the sheet is reduced (Fig. 40,b), and at a definite value of this quantity, the sheet breaks up into drops right at the outlet from the nozzle (Fig. 40,c).

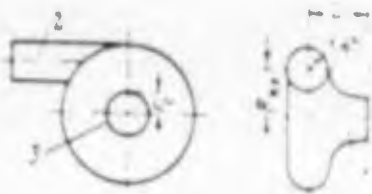


Fig. 39. Centrifugal injector.  
1 -- injector, 2 -- inlet, 3--  
outlet.

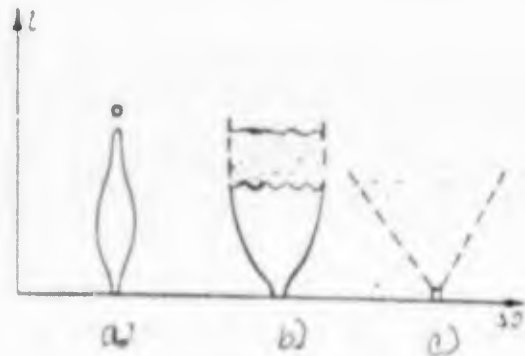


Fig. 40. Form of jet flowing  
out of centrifugal injector.



Fig. 41. Comparison of results  
of calculation with experimental  
data.

KEY: (a) Experimental points;  
(b) Theoretical dependence; (c)

From the simplest energy considerations [89], there can be obtained an expression for average diameter of drops formed during atomization of liquid in centrifugal injector:

$$d_{cp} = \frac{3}{\sqrt{2}} \sqrt{\frac{\sigma \cdot \eta}{PR_{01}}} \quad (4.6)$$

From this formula it follows that diameter of drop diminishes with increase of pressure. Besides, diameter of drop depends on surface tension of liquid,



increasing with increase of the latter, but it does not depend on density of liquid. From equation (4.6) it follows also that average diameter of drop does not depend on dimensions of outlet aperture of injector, but to a great extent depends on dimensions of tangential aperture at inlet into injector and on the radius of its internal chamber. Comparison of results of calculation with experimental data is shown in Fig. 41.

### 3. Characteristics of Atomization

During injection of fuel into combustion chamber, it breaks up into a huge number of drops with different diameters. Magnitude of average diameter of majority of drops characterizes fineness of atomization. Dimension of drops is determined experimentally. At present there have been developed a number of methods which are useful for measurement of diameters of drops and comparison of different atomizing mechanisms [90] [91].

From the proposed methods those in which there are used phenomena of dispersion, absorption and diffraction of light have the advantages, since in them the form of the spray in the combustion chamber is not distorted. Replacement of objective of camera by microscope allows one to directly measure magnitude of drop. There has been developed an electronic apparatus with computing mechanism, which significantly accelerates estimate of distribution of drops in the spray. Quality of atomization is characterized by distribution curve of drops. This curve is constructed so that along axis of the abscissa is plotted diameter of drops in microns, and along axis of ordinates — percentage number of drops of given diameter from the total number, which is taken as 100%. Ordinate of any point of such a curve shows percentage content of drops of a given diameter.

Analytical investigations [92] of the process of atomization show that distribution curve with a sufficient degree of accuracy can be characterized by an exponential curve for distribution of drops with respect to their number in separate groups

$$N_x = 1 - \exp\left(-\frac{x}{x_0}\right)^m, \quad (4.7)$$

as well as for distribution with respect to volume

$$\Omega_y = 1 - \exp\left(-\frac{y}{y_0}\right)^n, \quad (4.8)$$

where  $N_x$  and  $\Omega_y$  are fractions with respect to number and volume of drops with diameter smaller than  $x$  and  $y$ ;  $x_0$  and  $y_0$  represent the diameter of drops for which  $N_x = \Omega_y = 1 - e^{-0.368}$  or the diameter of drops whose number (volume) constitutes 36.8% of the total quantity of drops of the injected fuel. Ratio  $x/\bar{x}$  characterizes fineness of atomization, and  $m$  and  $n$  give an idea of the homogeneity of atomization.

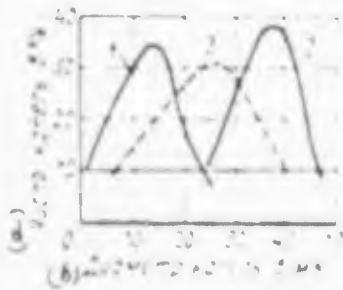


Fig. 42. Characteristic of atomization.  
KEY: (a) Number of drops in %; (b) Diameter of drops in  $\mu$ .

In Fig. 42 are illustrated three characteristics of atomization. The curve which goes up and down steeply corresponds to most uniform atomization. Curve which goes up and down with gentler slope corresponds to nonuniform atomization. The nearer the peak of a curve to the origin of coordinates, the finer the atomization.

Curves 1 and 2 show more uniform atomization than curve 3, but curve 3 represents finer atomization than curve 2. Fine and uniform atomization is shown by curve 1.

Fineness and homogeneity of atomization is affected by various factors. Investigations show that fineness, as well as homogeneity of atomization, increase with increase of pressure of injection. Increase of density of medium where injection is produced leads to growth of resistance of medium, which promotes faster disintegration of the jet. However, excessive increase of counterpressure can lead to negative results. Increase of viscosity of fuel also negatively affects atomization.

Besides the above presented parameters, the spray of atomized fuel is characterized also by the depth of its penetration into the combustion chamber.

The front of the spray consists of the totality of drops of a definite structure. Study of principles of motion of these drops presents special interest, since ignition of the mixture occurs on the front of the spray.

Equation of motion a drop [93] on the basis of data concerning drag coefficients of spheres in a motionless medium can be written in the form

$$-\frac{dv}{dt} = 0,75 \frac{\gamma_c}{\gamma_k} \frac{C}{d} \quad (4.9)$$

where  $v$  — velocity of drop;

$d$  — diameter of drop;

$\gamma_c$  and  $\gamma_k$  — specific gravities of medium and fuel respectively;

$C$  — drag coefficient. Value of this coefficient is given in the form of graphs  $\log C = f(\log Re)$ , where  $Re$ —Reynolds number.

The most simple solution is obtained on the assumption

$$C = 12,5 Re^{-0,5}.$$

Equation (4.9) can be reduced to the form

$$-\frac{d Re}{dt} = 2k Re^{1,5}, \quad (4.10)$$

where

$$k = 46 \frac{\gamma_c}{\gamma_k d^2}.$$

Integration of this equation on the assumption that diameter of drop  $d$ , its specific gravity  $\gamma_k$  and viscosity of medium  $\eta_c$  remains constant, gives

$$Re^{-0,5} - Re_0^{-0,5} = kt \quad (4.11)$$

or

$$v^{-0,5} - v_0^{-0,5} = kt, \quad (4.12)$$

where  $Re_0$  — value of Reynolds number  $t = 0$  and initial velocity  $V_0$ , and

$$k = 4,7 \frac{\gamma_c}{\gamma_k} \frac{v_0^{0,5}}{d^{1,5}}, \quad (4.13)$$

where  $\nu$  — kinematic viscosity.

Obtained equations (4.11) and (4.12) give dependence of momentum of drop on time for definite initial conditions.

In Fig. 43 is shown change of momentum of drops 10 and 20  $\mu$  in diameter in air at a pressure of 30 atm(abs) and temperature of 500° C for initial momentum

$v = 100$  m/sec. From Fig. 43 it is clear that momentum falls very rapidly and already in  $0.2 \cdot 10^{-3}$  sec drops of diameter  $10\mu$  practically completely lose their velocity, and further movement occurs together with the created flow of air.

In combustion chamber of liquid-fuel rocket engine, injection of fuel occurs at a velocity which is significantly less than that shown above; diameter of drops is significantly greater; therefore time of flight of drop in chamber of liquid-fuel rocket engine will be less than  $0.2 \cdot 10^{-3}$  sec.

It is possible to show that from equation (4.9) it is easy to obtain length of penetration of drop. For this it is necessary to place  $\frac{dL}{d\tau}$  into the equation instead of  $v$ , i.e., derivative of path with respect to time, and by means of integration of the obtained equation to obtain the value for depth of penetration of drop.

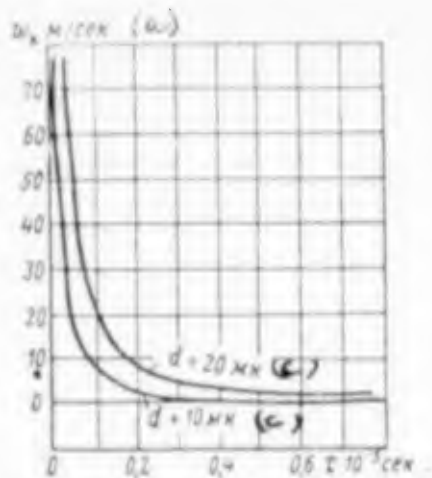


Fig. 43. Dependence of momentum drop on time.  
KEY: (a) m/sec; (b) sec;  
(c)  $\mu$ .

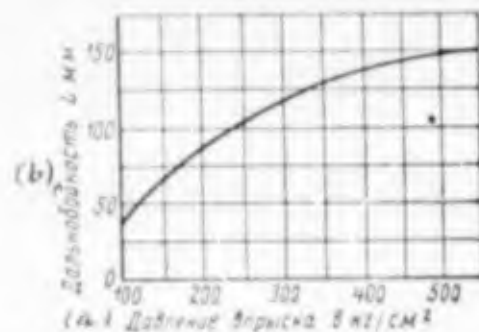


Fig. 44. Dependence of range of jet on pressure of injection.  
KEY: (a) Pressure of injection in  $\text{kg}/\text{cm}^2$ ; (b) Range mm.

Experimental dependence of range of jet on pressure of injection is shown in Fig. 44. Range of jet is influenced also by diameter of nozzle of injector and density of fuel. Decrease of diameter of nozzle decreases range of jet, and increase of density and renders opposite effect.

#### 4. Modeling of Process of Atomization

Process of atomization of fuel in combustion chamber depending upon design features of fuel supply system and operating conditions of motor is developed in

manifold forms. Therefore, investigations of such a process depend on the set of individual peculiarities which are inherent in the given hydrodynamic situation.

In this case it is most correct to seek a basis for investigations and quantitative generalizations by means of creation of a model of the phenomenon and description of it with the help of a system of differential equations. Only thus can there be obtained conclusions having practical value.

In principle, practical realization of such a method is connected with difficulties of construction of an undistorted model of the phenomenon and mathematical difficulties of solution of a system of differential equations, which would be possible in the future to use for practical problems. This method is not unique.

Since mathematical analysis of physical phenomena occurring during disintegration of the jet or sheet usually lead to complicated equations, strict solution of which is impossible; then process is described with the help of criteria of similarity, composed of physical parameters having an effect on the process. Both methods found application during the study of atomization.

In use of first method we proceed in the following way: on surface of jet of given form is placed an arbitrarily small perturbation and is studied influence of this perturbation. Thus it is assumed that all variables connected with the disturbance, are small compared to corresponding quantities defining the jet (radius, speed etc).

Since magnitude of perturbation is not stipulated, result of such analysis is reduced usually to conditions at the limit of stability of the stream [86].

Let us consider application of the second method.

In the process of disintegration of jet, the following forces are essential: force of inertia of liquid, surface force, force of viscosity of liquid and force of inertia of medium. All these forces can be combined in dimensionless criteria, characterizing turbulence, viscosity and aerodynamic forces. Such an analysis is carried out in work [94].

Postulating that turbulent motion of jet is the main factor of its disintegration, there can be obtained a simplified criterial equation for calculation of average diameter of drops and processing of experimental results [95, 96].

If we assume that a spherical volume of liquid of diameter  $D_0$  moves with velocity  $u_0$ , then condition of continuity of this volume will be the equality of kinetic energy and work of forces of viscosity and surface tension:

$$\frac{\rho u_0^3 D_0}{2} \sim \eta D_0 u_0 \sim \sigma D_0^2 \quad (4.14)$$

Dividing right side of expression (14) by the average we obtain

$$\frac{\eta}{\rho u_0 D_0} + \frac{\sigma}{\rho u_0^2 D_0} \approx 1 \quad (4.15)$$

or in criteria of similarity

$$\frac{1}{Re} + We \approx 1. \quad (4.16)$$

Equation (4.16) determines dimensions of drops obtained during break up of stream of diameter  $D$ , moving with velocity  $u$ :

$$D_0 \approx \frac{\eta^3 D^4}{\rho^3 u^3} + \frac{\sigma^{3.5} D^{2.5}}{\rho^3 u^{0.5}} \quad (4.17)$$

One should note that at the contemporary level of knowledge in the area of atomization of fuel, the assumption that it is possible theoretically to encompass the interaction of forces having influence on atomization scarcely will be justified. In spite of this, further experiments and theoretical investigations will make it possible to obtain satisfactory solution of this problem.

## Section 2. Evaporation of Fuel

During preparation of mixture for ignition and combustion, the process of evaporation of the fuel is the most important, since ignition and combustion of fuel occurs in the vapor phase; therefore, timeliness of formation of combustible mixture, completeness of combustion, and also structural elements of combustion chamber are in strong dependence on the volatility of the fuel.

Process of evaporation is a complicated physical process. Its complexity consists in that evaporation of fuel should be completed in a very small interval



of time (4 - 8 millineconds). In a motor usually are evaporated not individual chemical substances, but complicated, multicomponent liquids with different physical properties. Besides, it is necessary to consider the circumstance that process of evaporation under steady-state operating conditions of the motor, under the conditions of turbulent flow to a significant degree is determined by the intensity of heat transfer from surrounding combustion products to drops, which is quite difficult to estimate.

In spite of complexity of process of evaporation, the necessity for creation of economical motors and development of more efficient fuels absolutely require study of principles of evaporation in motors. In some investigations, theory of process of evaporation has been successfully combined with theory of heat transfer and hydrodynamics and valuable results have been obtained, which reveal the mechanism of evaporation of drops directly in motors.

#### 1. Isothermal Evaporation of Drops

As a result of the large temperature gradient between medium and drops of atomized fuel in pre-ignition zone of combustion chamber, there occurs intense heating and evaporation of drops. Rate of heating and evaporation depend mainly on dimension of drops, velocity of their motion relative to flow and on the intensity of chemical reactions proceeding in the liquid phase. In the latter case, the released heat accelerates heating and evaporation of fuel. Due to diffusion and motion of drops in flow, vapors of fuels formed on surface of drops are spread throughout the volume, and retard evaporation of drops of large size. Picture of further evaporation is abruptly complicated due to radiation of heat from the front of the flame.

Process of evaporation of drops is essentially distinguished from evaporation from large surfaces and is determined by the laws of hydrodynamics, heat transfer, and also physicochemical properties of the fuel.

Depending upon temperatures of drops and medium, process of evaporation has various characters. If temperature of drop is less than temperature of medium, flow of heat is directed from front of flame to evaporated liquid. This form of evaporation is characteristic for initial moment of injection of components into combustion chamber. In this period of time, drops are heated and temperatures are equalized.

As investigations of D. N. Vyrubov show [93], this period of time is not long continued and occurs at variable coefficient of heat transfer. Thus, for a drop of diameter  $20 \mu$ , this time constitutes  $0.6 \cdot 10^{-3}$  sec, and for a drop of  $10 \mu$  — —  $0.2 \cdot 10^{-3}$  sec. This time coincides with time of deceleration of drop. Under the conditions of the liquid-fuel rocket engine temperature of medium is higher; therefore it is necessary to assume that time of preliminary heating of drop in liquid-fuel rocket engine will be still smaller; the process of evaporation occupies an incomparably larger time.

A second case of evaporation is possible, when temperature of medium is less than temperature of drop. This is observed in pipe lines of motors with ignition from spark, and is not considered by us.

At last, the most simple case is evaporation during equality of temperatures of drop and medium into which fuel is injected. In this case thermal flux is absent and there takes place only diffusion of vapors.

The hypothesis, taken on the basis of calculations and theoretical assumptions [97], [98] that drops quite rapidly acquire the temperature of their environment and that the subsequent process of evaporation occurs under isothermal conditions, allows us to estimate influence of various factors on process of evaporation. The assumption concerning isometric equilibrium evaporation of the drop and disregarding of characteristics of heat exchange in the period of deceleration of drops allows us to consider that the process of evaporation proceeds under the conditions of molecular diffusion and heat transfer by thermal conduction. Thermal balance, composed for a drop of fuel, allows us to determine equilibrium temperature of evaporation.

Quantity of heat which is supplied to the drop can be expressed by the equation

$$Q_1 = \alpha(t_1 - t_2)F. \quad (4.18)$$

where  $\alpha$  -- heat-transfer coefficient;

$(t_1 - t_2)$  -- difference of temperature between medium and surface of drop  
(temperature of evaporation);

$F$  -- surface of drop

Quantity of heat expended on evaporation:

$$Q_2 = \beta \Delta p F l. \quad (4.19)$$

where  $\beta$  -- coefficient of evaporation in terms of difference in partial pressures;

$\Delta p = p_s - p_0$  -- difference in partial pressures: between pressure  $p_s$  on surface of drop corresponding to temperature of evaporation, and  $p_0$ , which is temperature of surrounding medium;

$l$  -- heat of evaporation.

Equating  $Q_1$  and  $Q_2$  and considering  $p_0 = 0$ , we obtain

$$\alpha(t_1 - t_2) = \beta p_s l. \quad (4.20)$$

Under the conditions of molecular diffusion and transmission of heat by means of thermal conduction, the minimum value of Nusselt's number for a drop of spherical form is determined by

$$Nu = \frac{\beta d}{D_p} = 2 \quad (4.21)$$

and

$$Nu = \frac{\alpha d}{\lambda} \quad (4.22)$$

where  $d$  -- diameter of drop;

$D_p$  -- diffusion coefficient of vapors;

$\lambda$  -- coefficient of thermal conductivity of medium.

From equations (4.20) -- (4.22) it follows that

$$\lambda(t_1 - t_2) = D_p p_s l. \quad (4.23)$$

Equation (4.23) is the main equation for determination of temperature of drop; thus, it is necessary to know diffusion coefficient  $D_p$  and dependence of  $p_s$  on temperature.

Quantities  $\lambda$  and  $\lambda$  for vapors of different fuels and their dependence on temperature are taken from the tables of physical quantities.

Diffusion coefficient is determined from the equation

$$D_p = D_{p,0} \left( \frac{t_c}{273} \right)^2 \frac{1}{p_c} \quad (4.24)$$

where  $D_{p,0}$  — diffusion coefficient at 0°C and 1 atm (abs);

$p_c$  — pressure of environment in atm (abs).

Dependence of pressure of saturated vapor on temperature is expressed by the equation

$$p_s = A e^{-B/t_c} \quad (4.25)$$

where A and B are constants characterizing properties of evaporated liquid;

calculation of these quantities is presented in work [122].

Substituting value of (4.24) and (4.25) into the equation (4.23), we will find

$$\lambda (t_c - t_s) = D_{p,0} \frac{t_c + 273}{273} \frac{1}{p_c} A e^{-B/t_c} \quad (4.26)$$

Equation (4.26) serves for finding of temperature of evaporation of drop.

Quantity of evaporated fuel can be written in the form

$$d(i) = \beta F (p_s - p_0) dt_c \quad (4.27)$$

Considering partial pressure of vapors of evaporated liquid in surrounding medium  $p_0 = 0$ , we obtain

$$\frac{d(i)}{dt_c} = \beta F p_s \quad (4.28)$$

Under the conditions of molecular diffusion

$$\beta = \frac{2D_p}{d} \quad (4.29)$$

then, equation (4.28) will be rewritten as

$$\gamma_s \frac{dV}{dt_c} = - \frac{2D_p}{2r} \pi (2r)^2 p_s \quad (4.30)$$

where  $V$  — volume of drop;

$\gamma_s$  — density of drop;

$r$  — radius of drop;

$\tau$  — time.

It follows from this that

$$\frac{d(r^2)}{d\tau} = -\frac{2D_p p_s}{\gamma_m} = \text{const.} \quad (4.31)$$

Consequently, the magnitude of the surface of the evaporating drop changes linearly in time. This dependence was experimentally obtained by Sreznevskiy [99] and several other investigators [100].

From equation (4.27) it is easy to obtain rate of evaporation

$$\frac{d}{d\tau}(d^3) = k' d\tau, \quad (4.32)$$

where  $k'$  for conditions of isothermal evaporation equals

$$k' = \frac{12D_p}{\gamma_m} p_s = \text{const.}$$

Integrating equation (4.32), we obtain equation of dependence of change of dimensions of drop in time

$$d_1^2 = d_0^2 - k\tau, \quad (4.33)$$

where

$$k = \frac{2}{3} k' = \frac{8D_p p_s}{\gamma_m}; \quad (4.34)$$

$d_0$  and  $d_1$  — diameters of drop in initial moment of time and after interval of time  $\tau$ .

At  $d_1 = 0$ , time of total evaporation of drop

$$\tau_0 = \frac{d_0^2}{k} = \frac{d_0^2 \gamma_m}{8D_p p_s}. \quad (4.35)$$

Time of partial evaporation

$$\tau = \tau_0 [1 - (1 - \Omega_{\text{evn}})^{2/3}]. \quad (4.36)$$

where  $\Omega_{\text{evn}}$  is the degree of evaporation in fractions of the initial volume.

Equation (4.33) shows that the quantity  $k$  represents rate of decrease of surface of drop and characterizes rate of evaporation.

Analysis of dependence of rate of evaporation and temperature of drops on temperature of medium and pressure, carried out in works [93], [101], [102], showed that with increase of temperature of medium in which evaporation occurs, temperature of drop increases and correspondingly evaporation is accelerated; thus for  $k$  and

$t_w$  there is obtained a linear dependence on the temperature of the medium. Increase of pressure of medium at constant temperature retards evaporation of drop.

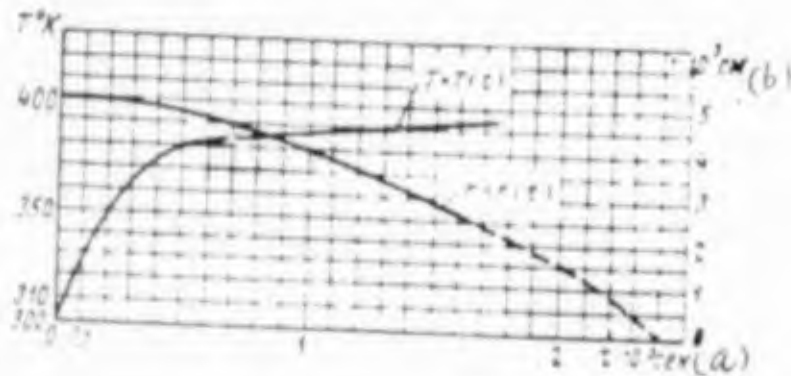


Fig. 45. Dependence of temperature and radius of drop of aniline in nitric acid motor ( $T_k = 3000^\circ\text{K}$ ,  $T_{vpr} = 300^\circ\text{K}$ ,  $r_0 = 10^{-3}\text{cm}$ ).  
KEY: (a) sec; (b) cm.

Investigations carried out by Leonov [103], [104] confirmed the possibility of acceptance of the assumption concerning isothermicity of process of evaporation and made it possible to develop a simplified method of estimate of volatility of Diesel engine fuels.

In Fig. 45 are presented curves of isothermal evaporation of drops, which were obtained by Penner [105], for aniline in a nitric acid motor, with velocity of injection 30 m/sec, and in Table 10 are presented values of time necessary for decrease of diameter of drop by one half.

Table 10.

(a) Наименование топлива	(b) $d_0 \cdot 10^3$ см	(c) $t_{(1/2)}$ , $10^6$ сек.
(d) Анилин ( $\text{C}_6\text{H}_5\text{NH}_2$ )	5	0,158
	10	0,500
(e) Октан ( $\text{C}_8\text{H}_{18}$ )	5	0,052
	10	0,188
(f) Гидразин ( $\text{N}_2\text{H}_4$ )	10	1,07

KEY: (a) Designation of fuel; (b)  $d_0 \cdot 10^3$  cm; (c) Sec; (d) Aniline ( $\text{C}_6\text{H}_5\text{NH}_2$ ); (e) Octane ( $\text{C}_8\text{H}_{18}$ ); (f) Hydrazine ( $\text{N}_2\text{H}_4$ ).



As can be seen from Table 10, the total time of evaporation of drops is different and strongly depends on the chemical nature of the fuel.

Thus, for example, time of evaporation of drops of aniline (diameter of drop  $5 \cdot 10^{-3}$  cm) constitutes nearly  $1.5 \cdot 10^{-3}$  sec, and drops of octane  $0.5 \cdot 10^{-3}$  sec. Time of evaporation of such fuels as aniline and hydrazine constitutes nearly 50% of the total time of conversion of fuel. Therefore, in motors which are designed for operation with such fuels, there should be provided for formation of drops of smaller diameter; otherwise, there will be observed drop in efficiency of the motor [105].

Consequently, volatility of drops of fuel has an important effect on flow of processes of fuel atomization and combustion in liquid-fuel rocket engine.

In an actual motor, there is evaporated a large number of drops of different diameters. Evaporation of this group of drops differs from evaporation of a single drop and depends to a strong extent on the character of atomization. However, the considered scheme of evaporation allows us to approach calculation of the aggregate of the large number of drops of different diameters.

## 2. Evaporation of Totality of Drops

Injection of fuel and oxidizer into combustion chamber in practice is accompanied by formation of drops of various dimensions; therefore, evaporation of this group of drops presents interest. Below we will consider the most simple case, in which the fuel is evaporated in a medium of evaporated oxidizer [97]. Distribution curve of diameters of drops obtained during atomization of fuel is described by the function

$$\Omega = \exp(-\xi^3), \quad (4.37)$$

where  $\xi = x/\bar{x}$  — relative dimension of drop;

$\Omega$  — volume (weight) fraction of drops whose dimension is larger than  $\bar{x}$ ;

$\lambda$  — characteristic of dimension, which is the diameter of drops for which  $\Omega = 1/e = 0.368$  and which determines the fineness of atomization;

$n$  — characteristic of distribution, determining uniformity of atomization. Value of this characteristic usually changes from 2 to 4.

Consequently, quality of atomization is characterized by two experimental constants: by the characteristic of dimension and the characteristic of distribution. First characteristic gives an idea of fineness of atomization, the second — of uniformity of atomization.

Number of drops of dimension  $x$  formed during injection of unit of volume of fuel can be obtained by means of differentiation of equation (4.37) with subsequent division of the obtained expression by volume of a drop of the corresponding diameter:

$$dN_x = \frac{G}{\pi} (-n) \frac{\lambda^{n-1}}{x^n} \exp\left(-\frac{\lambda}{x}\right)^n dx. \quad (4.38)$$

As a result of evaporation, the size of these drops will be decreased according to expression (4.33) to the size

$$d = \lambda \sqrt{d^2 - kt},$$

and volume of each drop will be

$$V_x = \frac{\pi}{6} (d^2 - kt)^3. \quad (4.39)$$

Drops, having dimension less than  $\sqrt{kt}$ , completely are evaporated and the remaining volume of fuel will be composed only of drops with dimension larger than

$\sqrt{kt}$ . Volume fraction of unevaporated fuel by the moment of time  $\tau$  will be

$$\Omega_{0,\tau} = \int_{\sqrt{kt}}^{\infty} (-n) \frac{\lambda^{n-1}}{x^n} (x^2 - kt)^3 \exp\left(-\frac{\lambda}{x}\right)^n dx. \quad (4.40)$$

Graphic integration of equation (4.40) can be carried out under the assumption that  $\lambda$  and  $n$  do not depend on time.

As investigations showed, values of  $n$  weakly affect course of curves

$$\Omega = f(b).$$

where

$$b = \sqrt{k \tau}$$

and therefore it is possible to assume that in the process of evaporation  $n$  remains constant.

For calculation of time of evaporation of a given fraction of fuel according to curve  $\Omega = f(b)$ , there is determined the corresponding value of parameter  $b$  at characteristic of distribution  $n$ , given by conditions of atomization and design of injector. Further is determined time of evaporation

$$\tau = \frac{b^2}{k} \quad (4.41)$$

and initial dimension of the drops which were completely evaporated during this time:

$$x_{\text{min}} \leq b x \quad (4.42)$$

As calculations show, during evaporation of totality of drops of different dimensions, quantity of evaporated fuel in the first period of evaporation significantly exceeds the quantity which is evaporated with drops of the same dimension. However, evaporation of totality of drops in the final period is strongly reduced.

Analysis shows that at large characteristics of distribution, totality of drops will consist of numerous liquid nuclei which are near in dimensions, surrounded by shells of vapors; at small characteristics of distribution, there will be small clouds of vapors and separate large liquid nuclei, surrounded by a layer of vapors. In the last case, there is the probability of formation of an overenriched zone, which leads to impairment of combustion.

Analysis described above, is complicated as a result of interaction of drops and chemical processes proceeding in the zone of vapor and there are required further theoretical and experimental investigations of the process of evaporation.

### Section 3. Mixing

The complex of phenomena which are usually associated under the name of fuel atomization includes not only atomization and evaporation of fuel, but also phenomena of mixing.

As a result of atomization and evaporation, in the combustion chamber will be created vapors of components, which by means of interdiffusion and heat exchange will form a combustible mixture.

Time necessary for formation of such a mixture and its concentration limits determine place of location of flame kernel and its stability.

Due to heterogeneity of atomization and different rates of evaporation of components, process of mixing is not completed in the pre-ignition zone, but is continued further into the zone of flame. Thus, the intensity of the process of mixing, due to the great difference in temperatures of the zone of flame and the pre-ignition zone, is extraordinarily great.

In the zone of flame, the process of mixing proceeds in parallel with burning and is completed in a distance which is small compared with the length of the combustion chamber.

Specific gravities of every zone separately for spontaneously inflammable and non-spontaneously inflammable fuel compositions are different. In the first case the main quantity of heat necessary for evaporation and creation of fuel mixture will be released directly during contact of two liquid phases; in the second case the fuel receives heat only from the source of ignition, and naturally one should expect a difference in the mechanism of mixing. In connection with the fact that this region has been insufficiently investigated, it is difficult to give the separate schemes of mixing for these two forms of fuel compositions.

Mixing of components in the pre-ignition zone, and also in the zone of burning has a clearly expressed hydrodynamic character and is determined by conditions of motion, diffusion and heat exchange.

Transfer of mass and heat transfer are similar processes and are described by one and the same class of differential equations. Main law of transmission of heat in a motionless medium is the law of Fourier, according to which heat flow is proportional to the gradient of temperatures

$$q = -\lambda \frac{dT}{dx} \quad (4.43)$$

where  $q$  — quantity of heat transmitted through a unit surface per unit of time;

$dT/dx$  — temperature gradient;

$\lambda$  — coefficient of thermal conductivity.

Corresponding law for diffusion will be the law of Fick, according to which diffusion flow is proportional to the gradient of concentration

$$q' = -D \frac{dc}{dx} \quad (4.44)$$

where  $q'$  — quantity of mass transferred per unit time;

$c$  — concentration of diffusing substance;

$D$  — diffusion coefficient.

Processes of transfer of heat and transfer of mass, which are described by equations (4.43) and (4.44) are observed only in solid bodies. In liquids and gases these processes are described in terms of laws of motion of a gas or liquid.

Under these conditions laws of Fourier and Fick should be augmented by terms which take into account velocity of motion of the flow; thus, for example, differential equation of transport of mass will be

$$q' = -D \frac{dc}{dx} + V_x c \quad (4.45)$$

where  $V_x$  — is component of velocity of flow in direction of axis  $x$ .

Direct use of transport equations for heat and mass for creation of method of calculation of fuel atomization leads to serious and unsolvable difficulties, even under conditions which are significantly simpler than conditions of mixing in liquid-fuel rocket engine. Problem is significantly simplified if we assume that due to a large number of factors having an influence on mixing, it is possible to select one which is decisive, and disregard the remaining ones. In this case it is possible to solve the problem; however, the large number of different factors and assumptions leads to significant conditionality of the obtained solutions.

In the preface to work [139], we noted that for understanding of the process of burning in liquid-propellant rocket engine, an important value is attributed to contemporary ideas of diffusion theory of burning of an atomized fuel. To this

theory we will return in Chapter VI. Here let us note that in this theory, a leading role is played by the idea that the total process of burning of atomized fuel can be schematically divided into two stages: mixing of components of fuel mixture, and chemical reactions of burning.

In forced chambers, chemical reactions due to high temperatures occur practically instantaneously, and, consequently, increase of rate of burning is limited by mixing, and it will be attained under the action of turbulence.

Burning, with which the rate of the process is limited by mixing, according to accepted terminology is called diffusion burning [52], [106].

In works of Frank-Kamenetskiy was proposed a division of diffusion burning into two types—"mac-rodiffusion", when burning occurs on the boundary of large gas volumes, and "micro-diffusion" burning, when fuel and oxidizer make up a mixture of small volumes and, consequently, mixing is observed not on a fixed boundary, but throughout the entire volume.

In both cases mixing occurs by means of turbulence. During small-scale turbulence, mixing always occurs by means of molecular diffusion and the size of the broken up volumes is less than the scale of turbulence.

Time of mixing will be expressed as:

$$\tau = \frac{\delta^2}{D} \quad (4.46)$$

where  $\delta$  — average size of broken up volume and

$D$  — diffusion coefficient.

In the case when dimensions of broken up volumes are larger than the scale of turbulence, mixing occurs by means of turbulent diffusion and the role of the diffusion coefficient will be played by the coefficient of turbulent exchange  $A$ .

In liquid-propellant rocket engines there always takes place turbulent flow and preliminary splitting up of components; therefore, it is possible to consider that mixing with the help of turbulent diffusion is the most wide-spread during burning of fuel in these motors.



If the process of mixing of the oxidizer of the fuel is characterized by turbulent diffusion and the average dimension of their gas volumes, then, from considerations of dimension, the time of mixing, with accuracy up to the constant factor, will be

$$\tau \approx \frac{l}{D_T} \quad (4.47)$$

Intensity of such a form of mixing in the first approximation is determined by the Reynolds number of the gas flow.

Scale of splitting up  $\delta$  is determined by design and regime parameters of the propulsion system, and coefficient of turbulent diffusion — by the following approximate:

$$\frac{D_T}{D} \approx \frac{Re}{Re_{kp}} \quad (4.48)$$

where  $D$  is the coefficient of molecular diffusion, and  $Re_{kp} \sim 2300$  (Fig. 46).

Determination of the order of the time of mixing, and also the character of its change depending upon structural and regime parameters, requires special experimental investigation under conditions near to the conditions in the motor.

Introduction of total effective characteristics, correctly representing principal aspects of the phenomenon of the process of mixing in a motor, is not the only way for discovery and development of a method of analysis of the process of mixing.

For generalization of experimental and theoretical investigations there can be used methods of the theory of similarity. With the help of dimensionless criteria of Nusselt and Margules, it is possible to describe processes of heat and mass transfer, but for definite geometric and physical conditions these criteria are functions of the criteria of Prandtl and Reynolds.

For the process of diffusion, the form of these criteria is as follows:

$$Nu = \frac{\beta l}{D}, \quad Ma = \frac{\beta}{v}, \quad Pr = \frac{\nu}{D}, \quad Re = \frac{vl}{\nu}$$

where  $\beta$  — rate constant of diffusion;  
 $v$  — velocity;

- $d$  — linear dimension;
- $\nu$  — kinematic viscosity;
- $D$  — diffusion coefficient.

In general form it is possible to write

$$Ma = \varphi(Re, Pr). \quad (4.49)$$

In a motionless medium or in laminar flow

$$Nu = f(Re, Pr). \quad (4.50)$$

Form of these dependences is determined experimentally. If such a dependence is established, then it is possible to carry out analysis of the process of mixing.

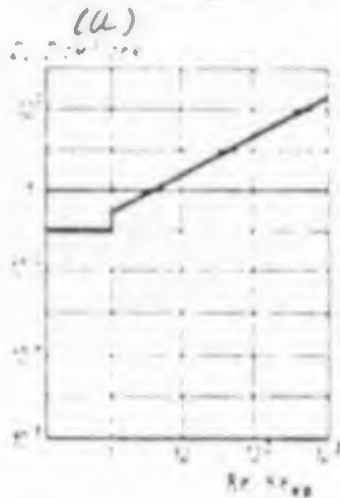


Fig. 46. Dependence of coefficient of turbulent diffusion on number  $Re$ .

KEY: (a)  $cm^2/sec$ .

#### Section 4. Delay of Ignition

It was shown that process of fuel atomization in combustion chamber is a complicated set of physical and chemical phenomena. Experimental study of this process presents large difficulties, but the complex study of phenomena proceeding in this case is almost impossible.

Together with this, discovery of the connection between the operating process of a motor with physicochemical properties of the fuel is fundamentally important from the point of view of perfection of designs of motors, as well as from the point of view of correct use of fuel. Therefore, in the course of a long period of time, there have been made attempts to find a total characteristic which could

evaluate the process of fuel atomization. In the area of motors with ignition due to pressure, where the process of burning proceeds under conditions very near to conditions in a combustion chamber of a liquid-fuel rocket engine, as such a characteristic was selected delay of ignition ( $\tau_3$ ).

Delay of ignition is the time which passes from the moment of injection of fuel, to the formation of the first focus of flame. Since the concept of delay of ignition for liquid-fuel rocket engine has approximately the same meaning as for motors with ignition due to pressure, methods of determination of this quantity, and also results of investigations in many respects coincide.

Methods of estimate of usefulness of fuels for motors with ignition due to pressure, in the process of their development, have undergone a number of serious changes. These changes basically are connected with the fact that between characteristics of fuels which are obtained by various laboratory methods, and the real behavior of the fuels in a motor, in many cases there were serious discrepancies. These discrepancies appeared as a result of differences in the conditions of occurrence of fuel of atomization in apparatuses for test of fuels and in conditions in an actual motor.

The standard method of evaluation of fuels which is applied at present for motors with ignition due pressure also does not reflect the real behavior of the fuel. Determination of delay of ignition by this method is conducted on a standard motor, and evaluation of fuel is produced by means of fuel equivalents (cetane numbers).

In the use of fuel equivalents, it is assumed that the sequence obtained for fuels of different chemical nature according to their inclination to ignite does not depend on design of the motor. However, as the practice of operation of motors with ignition due to pressure showed, for many designs fuel with large cetane number will behave worse than fuel with smaller cetane number. In high-speed motors cetane number has practically no value, since the time of chemical reactions for

present-day motors is extremely small compared to the time which the physical processes take, which limit fuel atomization. Under these conditions, time of delay of ignition is not a physicochemical constant, but depends on structural and regime parameters of the propulsion system.

In connection with this, in the area of motors with ignition due to pressure, there are being sought new ways for motor evaluation of fuels. Analogous picture is observed in the area of evaluation of fuels with the help of delay of ignition for a liquid-fuel rocket engine [107], [108].

Process of burning in chamber of liquid-fuel rocket engine proceeds at significantly higher temperature, and time of chemical reactions here is significantly less than in chamber of motor with ignition due to pressure. In the given case it is necessary to expect an even sharper disparity between evaluations obtained by laboratory methods and the behavior of fuel in actual motors.

For a liquid-fuel rocket engine operating on non-spontaneously inflammable fuels, time of delay of ignition in general does not have any meaning, since in this case it is necessary to use the concept of time of conversion of retardation. Time of delay of ignition has value for investigation of emergence of motor into operating conditions and for study of liquid-phase reactions [138], [139].

#### 1. Methods of Determination of Delay of Ignition

Determination of delay of ignition is produced by means of carrying out tests in a cup, by the drop method and in instruments built according to the principle of a rocket motor.

We will consider the first method. Into a cup is poured initially one component of the fuel, and then the second. Time from moment of contact of components to appearance of flame is recorded. Quantities obtained with the help of this method characterize physicochemical processes which proceed between fuel and oxidizer, and depend on conditions of mixing and quantities of components given in cup. This

method has value for qualitative evaluation of delay of ignition of different fuels and study of liquid-phase reactions.

In order to avoid errors, there was developed the drop method. It consists of the following: in the cup is located a drop of one component, and a drop of the second component falls into the cup onto the drop of the first component. Delay of ignition is determined from the moment of fall of the drop to the appearance of flame. Errors of measurement of the two described methods are very great, and only by means of statistics can there be obtained quantitative results concerning the character of the pre-ignition processes.

More improved instruments for study of delay of ignition are apparatuses in which oxidizer and fuel move in continuous flow from capillaries under atmospheric pressure. After meeting of the components there occurs mixing in the liquid phase, accompanied by violent exothermal reaction and their ignition.

One should note that chemical reactions in the liquid phase and processes of mixing to a strong degree depend on angle of encounter of components, and since this angle is determined by structural peculiarities of the apparatus, results obtained in such an apparatus are poorly reproducible.

A strong effect on results of measurements is rendered also by pressure and temperature; therefore, it is difficult to expect that results obtained in a motor could be compared with results obtained on such an apparatus.

Attempts to avoid these disadvantages led to creation of installations in which are simulated conditions of process of burning in an actual motor. Creation of micro-motors for study of delay of ignition also did not solve the problem of transfer of results obtained on small motors to actual motors. This is explained basically by the fact that micro-motors are different from actual motors with respect to the number of injector nozzles and the volume of chambers.

In Table 11 are presented results of measurements of delay of ignition, obtained by the method of the cup, the drop method, and also in small motors operating on nitric acid and aniline.

Table 11. Delay of Ignition for Nitric Acid and Aniline at Room Temperature and Atmospheric Pressure [182].

Задержка воспламенения (a) сек.	Тип прибора (b)
0,8 ± 0,12	(c) Метод чашки
0,003 ± 0,00	(d) Капельный метод
0,16	(e) Микроинжектор

KEY: (a) Delay of ignition in sec; (b) Type of instrument; (c) Method of the cup; (d) Drop method; (e) Micromotor.

As can be seen from this table, delay of ignition oscillates from 0.003 to 0.12 sec.

Analysis of data on delay of ignition from different instruments shows that the main cause determining such a scatter consists of the following: phenomena proceeding during the time of fuel atomization are basically explained by physical processes (atomization, evaporation, mixing, etc.) and therefore it is difficult to expect any conformity of measurements of delay of ignition in actual motors and in laboratory installations.

## 2. Factors Having an Effect on Delay of Ignition

Experimental data which were accumulated in the area of investigations of delay of ignition allow us to reveal the main factors having an effect on results of measurements of this quantity [108].

In Fig. 47 are presented results connected with ascertaining the influence of initial temperature on delay of ignition. As can be seen from Fig. 47, increase of temperature from 5 to 30 degrees C decreases delay of ignition by 2 times. There is still a whole series of investigations which show sensitivity of delay of ignition to temperature. However, it is difficult predict quantitative changes of delay of ignition depending upon temperature, since with change of the latter physical properties of fuel (viscosity, surface tension, etc.) change, thereby affecting fuel atomization. Delay of ignition is influenced also by pressure of injection,



since it depends on the square of velocity of injection.

There are relatively few works on the influence of hydrodynamic factors on delay of ignition. However, from discussion of mechanism of delay of ignition, it is obvious that changes of pressure of injection should affect the period of delay of ignition.

Besides the enumerated factors, delay of ignition depends also on initial pressure of medium into which injection of components is produced. For spontaneously inflammable fuels, delay of ignition strongly increases with decrease of pressure. This fact has special significance for process of ignition proceeding at high altitudes.

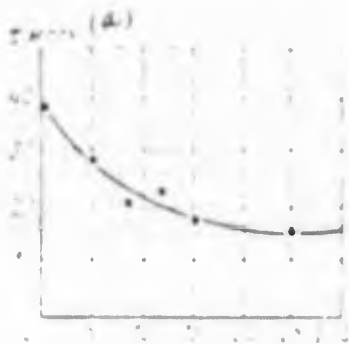


Fig. 47. Dependence of delay of ignition on temperature [108]  
KEY: (a) msec.

Delay of ignition depends also on composition of mixture. Minimum value of delay of ignition occurs at  $\alpha = 1.1$  to 1.2. Chemical nature of fuel renders important influence on magnitude of delay of ignition. Results of experiments which were conducted on a laboratory motor at pressure in combustion chamber  $p = 10 \text{ kg/cm}^2$  are presented in Table 12.

In Table 12 are presented delays of ignition mainly for fuels of the class of amines. Determination of delay of ignition in instruments of different designs show that unsaturated hydrocarbons with the allyl group are ignited with nitric acid, saturated hydrocarbons are not ignited with it. Aromatic ring in hydrocarbons can be activated by introduction of an atom of nitrogen or sulfur into the ring.

A strong influence on magnitude of delay of ignition is rendered by various additions to the fuel. Thus, for example, addition of small quantities of salts of copper or iron transforms non-self-igniting fuel — hydrazine hydrate + hydrogen peroxide into spontaneously inflammable fuel.

The presented data concerning dependence of delay of ignition on chemical structure of fuel have a qualitative character. Thus, all investigations in this region have been carried out under the conditions when it is difficult to separate the influence of chemical factors from that of hydrodynamic factors.

Table 12. Influence of Chemical Nature of Fuel on Delay of Ignition [108].

(a) Топливо	(b) Состав смеси	(c) Задержка воспламенения msec
(d) Фурфуроловая спирт + HNO <sub>3</sub>	1,21	33
(e) 25% анилина + 75% фурфуролового спирта + HNO <sub>3</sub>	1,31	18
(f) 25% диметиланилина + 75% фурфуролового спирта + HNO <sub>3</sub>	1,4	95
(g) 25% толuidина + 75% фурфуролового спирта + HNO <sub>3</sub>	1,3	37
(h) 25% ксилидина + 75% фурфуролового спирта + HNO <sub>3</sub>	1,4	20
(i) 50% ксилидина + 50% фурфуролового спирта + HNO <sub>3</sub>	1,57	27
(j) 25% диэтиламина + 75% фурфуролового спирта + HNO <sub>3</sub>	1,17	55
(k) 25% триэтиламина + 75% фурфуролового спирта + HNO <sub>3</sub>	1,75	61

KEY: (a) Fuel; (b) Composition of mixture; (c) Delay of ignition in msec; (d) Furfuryl alcohol + HNO<sub>3</sub>; (e) 25% aniline + 75% furfuryl alcohol + HNO<sub>3</sub>; (f) 25% dimethyl aniline + 75% furfuryl alcohol + HNO<sub>3</sub>; (g) 25% toluidine + 75% furfuryl alcohol + HNO<sub>3</sub>; (h) 25% xyloidine + 75% furfuryl alcohol + HNO<sub>3</sub>; (i) 50% xyloidine + 50% furfuryl alcohol + HNO<sub>3</sub>; (j) 25% diethyl amine + 75% furfuryl alcohol + HNO<sub>3</sub>; (k) 25% triethyl amine + 75% furfuryl alcohol + HNO<sub>3</sub>.

It is very difficult to obtain any data which have value for non-self-igniting fuels. Investigations in the area of study of delay of ignition of non-self-igniting fuels can have value only in the case when it is a question concerning selection of a method of ignition of the fuel. For these fuels, mixing in the liquid phase does not lead to any serious changes of pre-ignition reactions.

## CHAPTER V

### STEADY-STATE REGIME OF BURNING

Investigation of process of burning in liquid-propellant rocket engines has as its purpose to explain main mechanisms of conversion of initial components into products of combustion. Mechanism of conversion of fuel in the combustion chamber should show designers and chemical engineers ways for development of new, more efficient motors.

Separate supply of components, partial or complete combination of process of fuel atomization with process of burning seemingly associates liquid-propellant rocket engine with internal combustion motors and air-breathing jet engines. However, there are a number of features which are peculiar to the operating process in the liquid-fuel rocket engine. These features are the following: Kinetics of chemical reactions, due to high temperatures, proceeds with rates far exceeding rate of processes of burning in internal combustion engine and in air-breathing jet engine. Process of fuel atomization in these motors is the process of formation of a fuel mixture out of two liquid components. Heat-release rate in liquid propellant rocket motors is much greater than in other heat engines.

The enumerated features show that process of burning of fuel in liquid-propellant rocket engine is a new type of burning of atomized fuel.

Using present-day concepts of the diffusion theory of burning, there can be made a number of conclusions concerning observed phenomena in the combustion chamber, which have theoretical, as well as practical interest.

## Section 1. General Concepts

Propellant for liquid propellant rocket engine — fuel and oxidizer — regardless of the method of supply, proceed into the combustion chamber individually in the liquid state. Jets of fuel and oxidizer, under the influence of a whole series of factors, are broken up into separate small volumes and are distributed in the combustion chamber in the form of individual concentration zones. Their velocity of advance initially is different from the velocity of flow in the chamber, but at a small distance from the intake of the motor it becomes equal to the flow velocity. Depending upon construction of injectors, dimensions of these broken up volumes are different.

In the case of spontaneously inflammable fuel composition during contact of fuel with oxidizer there begin liquid-phase reactions, accelerating the process of heating, evaporation and further mixing of the components.

Nature of fuel vapor from the point of view of its inflammability is evident only in the initial stage of the process, during starting of the motor. In the steady-state regime, the presence of a thick flame, processes of fuel atomization in spontaneously inflammable and non-self-igniting fuel vapors are basically identical.

In places of contact of broken up volumes of fuel and oxidizer, under influence of temperature of medium, there begins process of mixing of vapors and formation of fuel mixture.

In this process there participates only an insignificant part of the fuel; the larger part of it, in the form of fuel fog, by flow passes to the front of the flame. Front of flame in this case is not a geometrical surface, separating fuel mixture from products of combustion, but is the extended, complicated form of the distributed zone of flame of definite width. In it there occurs sharp intermittent burning of the main mass of fuel, regardless of the aggregate state of the components which have entered it.

Such a character of burning of fuel is caused by the very high rate of chemical

reactions which take place in the chamber of a liquid-fuel rocket engine. Depending upon fineness and homogeneity of atomization, volatility of fuel and magnitude of turbulent diffusion, widths of this zone vary. The less complete the mixing, the wider the zone of burning and vice versa.

If increase of completeness of transformation of fuel in the combustion chamber depends on hydrodynamic factors/<sup>determining/</sup> fuel atomization, then, naturally there appears the question, where and when does the chemical nature of the fuel become important. Chemical nature of the fuel is important in two cases: during selection of fuel systems with high efficiency and during the necessity of providing for reliable emergence of the motor into operating conditions.

In the first case, i.e., during increase of efficiency of process by means of selection of oxidizer and fuel, chemical nature of fuel is manifested in the form of increase of specific thrust. Let us show this more specifically. Approximately, the thrust of a liquid-propellant rocket motor is determined as the root square of the difference of enthalpies of initial and final products of the reaction.

For determination of thrust of a motor it is necessary to know the rate of consumption of fuel and rate of outflow of gases. First quantity is determined by structural considerations; concerning the rate of outflow, it depends on physico-chemical state of products of combustion.

Expression for rate of expiration can be represented in the form

$$C = C_F C^* \sqrt{\frac{2kC}{k-1} \frac{R}{M} T_k \left[ 1 - \left( \frac{p_k}{p^*} \right)^{\frac{k-1}{k}} \right]} \quad (5.1)$$

where  $R$  — universal gas constant;

$k$  — index of polytropic curve;

$M$  — average molecular weight of products of combustion;

$T_k$  — temperature of gases in chamber;

$C_F$  — coefficient of thrust of motor.

Coefficient of thrust of motor very slightly depends on chemical nature of fuel and is mainly determined by design of motor. Value of coefficient  $C^*$  wholly is determined by the chemical nature of components and its maximum value is determined by the ratio  $T_k/M$  (see Table 13).

Table 13. Temperature in Combustion Chamber and Average Molecular Weight of Products of Combustion for Different Fuels at  $p_k = 36 \text{ kg/cm}^2$  [111].

(a)	Окислитель	(b)	Топливо	$T_k, K$	M	$C^*$	Температура продуктов сгорания
(b)	Перекись водорода	Бензин (f)	2180	21	1,2	218	
(b)	Перекись водорода	Гидразин (g)	2800	19	1,22	280	
(c)	Азотная кислота	Бензин (f)	3116	25	1,24	310	
(c)	Азотная кислота	Аммиак (i)	2533	—	—	253	
(c)	Азотная кислота	Аммиак (i)	2440	21	1,24	247	
(d)	Кислород	Спирт (j)	3041	22	1,22	309	
(d)	Кислород	Бензин (f)	2992	22	1,24	294	
(d)	Кислород	Гидразин (g)	3207	18	1,25	320	
(d)	Кислород	Водород (k)	2775	9,0	1,26	264	
(e)	Фтор	Аммиак (i)	4257	19	1,33	425	
(e)	Фтор	Гидразин (g)	4000	19	1,33	316	
(e)	Фтор	Водород (k)	2741	8,9	1,33	274	

KEY: (a) Oxidizer; (b) Hydrogen peroxide; (c) Nitric acid; (d) Oxygen; (e) Fluorine; (f) Gasoline; (g) Hydrazine; (h) Aniline; (i) Ammonia; (j) Alcohol; (k) Hydrogen; (l) Fuel; (m) Specific thrust in  $\text{kg}\cdot\text{sec}/\text{Kg}$ .

For temperature  $T_k$  there exists an upper limit, determined by physicochemical properties of components of products of combustion; regarding, however, the quantity M, it lies in practice within the limits 8.9—25. Upper limit for  $T_k$  and lower limit for M determine the range of possible application of chemical elements in fuel components.

Second case connected with manifestation of chemical nature of fuel concerns basically ensuring of reliable emergence of motor into operating conditions. It is known that for non-self-igniting fuels, stable burning is possible only in the



presence of a thick flame; in its absence ignition of this form of fuel becomes impossible.

Spontaneously inflammable components, due to high rates of liquid-phase reactions will release a large quantity of heat; the system does not need an external source of ignition, and emergence of the motor into the steady-state regime, thus is fully reliable. Thus, here is manifested the chemical nature of the fuel.

However, the last statement by no means is a specific property of spontaneously inflammable fuels and very frequently also is determined not only by the chemical nature of the fuels, but also depends on hydrodynamic conditions, which will be created in combustion chamber at the moment of starting.

There are known cases in the use of spontaneously inflammable fuels, when the motor does not emerge into operating conditions during injection of components through centrifugal injectors, and this completely reliably occurs on jet injectors. Reliable emergence of motor into operating conditions during supply of spontaneously inflammable fuel through jet injectors is explained by favorable local conditions of heat transfer for different volumes of fuel in the chamber [106], [107].

In the case of supply of the same fuel through centrifugal injectors, the intensity of cooling of separate location is so great that spontaneously inflammable fuel is not in the state to ensure reliable emergence of motor into operating conditions.

Significant interest for development of our knowledge concerning process of burning in liquid-fuel rocket engine is presented by works carried out in the area of study of operating process in motor with ignition due to pressure, and in particular by works connected with interpretation of M-process [113], [114].

Process of burning in motor with ignition due to pressure in these investigations is divided into two stages — multistage self-ignition with creation of volume location of burning and turbulent propagation of flame through a heterogenous charge.

These two phenomenon of the operating process in a motor with ignition due to

pressure very frequently are not bounded in time and in practice it can happen that after appearance of one location, there occurs formation of a whole series of locations of self-ignition and additional fronts of flame.

For realization of transition from self-ignition to turbulent propagation of flame, it is necessary to create a location of burning, dimensions of which are comparable with the scale of turbulence. Fraction of fuel which is necessary for such a primary location constitutes approximately 5% of all the entering fuel. Excess fuel entering during ignition into the combustion chamber is unnecessary and retards further development of the process.

For favorable development of second stage of burning, there is required equipartition of remaining quantity of fuel (95%) throughout volume of combustion chamber under influence of turbulent motion of gas; thus, the aggregate state of fuel renders only in insignificant influence on propagation of turbulent flame. Correct resolution of these two requirements leads to separate injection of fuel for self-ignition and for main burning.

Development of idea of two main stages, taking place during burning of atomized fuel, obtains special value not only for cyclic process, but also for understanding the process of ignition and burning in liquid-fuel rocket engine.

General presentations concerning process in combustion chamber allowed to explain that in spite of complexity of phenomena occurring in chamber of liquid-fuel rocket engine, it is possible to separate two main phenomena directing the process. The first of them carries a hydrodynamic character and determines stage of mixing of components, and the second determines chemical reactions of fuel components — properly burning. Interaction of speeds of these phenomena and specific peculiarities of such process are combined with diffusion theory of burning, main positions of which in reference to liquid-fuel rocket engine are outlined below.

General presentations concerning process of burning of fuel show that observed speed of burning in liquid-fuel rocket engine is determined, on the one hand, by

true speed of chemical reactions and, on the other hand, speed of delivery of reacting components to zone of flame.

Depending upon relationship of speeds determining condition of flow of process, it is possible to distinguish two maximum regions. In the first of them, the kinetic, the speed of reaction is much less than the diffusion rate of reacting components and observed speed of process coincides with true chemical reaction rate. In the second region — diffusion — speed of process is entirely determined by transfer of substance to zone of burning.

Such division of process of burning of atomized fuel lies at the basis of researches, in which a leading role is played by the presentation of the diffusion theory. Using the fundamental positions of this theory, it is possible to indicate a way for increase of speed of burning in reference to the liquid-fuel rocket engine. For the kinetic region, a decisive value is possessed by physicochemical constants of fuels, which are not typical for combustion chambers of air-breathing jet engine and liquid-fuel rocket engine and for engines with ignition by pressure.

In diffusion region, process of burning is limited by factors of hydrodynamic nature and first of all by mixing. Diffusion region of burning is observed in those cases, when chemical reactions due to high temperatures occur practically instantly and process is limited to mixing. This form of burning occurs in all engines where there exists separate supplying of components.

Let us consider solution of problem concerning detecting of stationary operating conditions of engine in diffusion region. We frequently noted that in process of burning of fuel it is possible to separate two stages — mixing and self-burning, and if in the form of first order of approximation we consider additive time of their flow, then

$$\tau_r \sim \tau_k + \tau_m, \quad (5.2)$$

where  $\tau_r$   $\tau_k$   $\tau_m$  are characteristic scales of full time of combustion, time of flow of chemical reactions and mixing, correspondingly.

For stationary method in liquid-fuel rocket engine, a decisive role is played by mixing, i.e., the region of diffusion burning, where

$$\tau_1 \gg \tau_2.$$

therefore

$$\tau_1 \sim \tau_2. \quad (5.3)$$

Time equation (5.2) has value during the study of conditions of ignition and extinction of process at the consideration of the second maximum region — kinetic, and also for case of intermediate regions of burning.

Time of turbulent burning, as it was shown in Chapter II, out of considerations of dimension will be

$$\tau_2 \sim \frac{l^2}{D_1}. \quad (5.4)$$

As is known, absolute value of this magnitude is determined by dimensions of primary splitting of components and coefficient of turbulent diffusion. Process of turbulent mixing and burning in combustion chamber due to its imperfection is extended. Quantitative effect of stationary process is characterized not only by time of burning, but also by the time used for it, i.e., time of stay of gases in chamber. Essential value has its ratio to time of burning [126]. Therefore, before we determine the condition of the stationary method, we will derive an equation for time of stay. Time of stay for single-pass combustion chamber is equal to the ratio of length of combustion chamber ( $L_k$ ) to average momentum of gases in it, consequently,

$$\tau_s = \frac{L_k}{W} \quad (5.5)$$

or

$$\tau_s = \frac{G_0}{G}, \quad (5.6)$$

where  $G$  is second expenditure of fuel;

$G_0$  is weight content of gases in chamber.

Time of stay is easy calculate from direct measurements of second expenditure of fuel and pressure in combustion chamber.

Second consumption of fuel

$$G = F_{*p} \gamma_{*p} W_{*p} = F_{*p} p_{*p} \sqrt{\frac{kR}{RT_{*p}}}; \quad (5.7)$$

since

$$p_{*p} = p_* \Gamma \quad \text{и} \quad T_{*p} = \frac{2T_*}{k+1},$$

then

$$G = F_{*p} \Gamma \sqrt{\frac{kR}{RT_*} p_*}, \quad (5.8)$$

where

$$\Gamma = \left( \frac{2}{k+1} \right)^{\frac{k+1}{2(k-1)}}.$$

In the stationary method of burning, the weight content of gases in chamber

$$G_0 = V_* \gamma = V_* \frac{p_*}{RT_*} = L_* F_* \frac{p_*}{RT_*},$$

where  $V$  is volume of combustion chamber;

$F_k$  is area of cross section;

$k$  is index of adiabatic line;

$R$  is gas constant;

$T$  is temperature;

$\gamma$  is density.

After conversions, we receive

$$\tau_n = \frac{1}{\Gamma} \frac{F_*}{F_{*p}} \frac{L_*}{a_*} = \frac{1}{\Gamma^2} \frac{F_*}{F_{*p}^2} \frac{1}{kR} \frac{L_0}{p_*}. \quad (5.9)$$

Let us note that with proportionality of pressure in chamber, the weight expenditure of time of stay remains constant.

It is easy to show that all that has been said remains correct for temperature and speed of gases in chamber:

$$T_* = \frac{F_{*p}^2 kR}{R} \Gamma^2 \left( \frac{p_*}{G} \right)^2 \quad (5.10)$$

and

$$W_* = \frac{F_{*p}^2}{F_*} kR \Gamma^2 \frac{p_*}{G}. \quad (5.11)$$

Time of turbulent burning is closely connected with coefficient of fullness of combustion, i.e., with conditions and structural parameters of engine, and allows

determination of conditions of stationariness of method during diffusion burning.

In the stationary method, the quantity of heat, which will emanate in combustion chamber due to chemical reactions, should be equal to the quantity of heat emitted by products of combustion from the chamber. Disturbance of this equality entails appearance of unstable methods. Method of researches of levels of stationary process of burning is considered by Simon in his classical theory of thermal explosion, and for the liquid-fuel rocket engine — in the works Vulis [106], [115], [116].

Degree of completeness of burning can be determined from the equation of thermal balance. The temperature of the burning in the chamber equals;

$$T_c = T_0 + \frac{q}{c_p} \quad (5.12)$$

whence

$$\theta = \frac{q}{q_0} (T_c - T_0) \quad (5.13)$$

or

$$\theta = \frac{1}{\beta} (\theta - 1), \quad (5.14)$$

where  $c_p$  and  $q$  is heat capacity and thermal effect of reactions, referred to a unit of mixture;

$T_0$  — initial temperature,

$$\beta = T_c - T_0 \text{ and } \theta = q / c_p T_0.$$

Expression (5.14) for determination of coefficient of fullness of combustion may be converted.

We shall substitute value  $T_k$  from equation (10), then

$$\theta = \frac{kC}{RT_0} \left[ 1 + \left( \frac{p_k F_{st}}{G} \right)^2 \right] \quad (5.15)$$

From the experiment, one can determine  $p_k$  and  $G$ ; therefore, we shall isolate from equation (5.15) the criterion having dimension of speed:

$$C = \frac{RT_0}{k} \left[ \theta - 1 + \left( \frac{p_k F_{st}}{G} \right)^2 \right] \quad (5.16)$$



or

$$C^* = \sqrt{\frac{2kT_0}{1+\alpha}} \quad (5.17)$$

Then expression for  $\eta$  will be

$$\eta = C^* \frac{F_{\text{exp}} - kT_0}{kT_0} \quad (5.18)$$

We shall substitute from equation (5.8) the value

$$C^* = \sqrt{\frac{2kT_0}{1+\alpha}}$$

then

$$\eta = C^* \frac{F_{\text{exp}} - kT_0}{kT_0} = \sqrt{\frac{2kT_0}{1+\alpha}} \frac{F_{\text{exp}} - kT_0}{kT_0}$$

where

$$C^* = \sqrt{\frac{2kT_0}{1+\alpha}} \quad (5.19)$$

therefore,

$$\eta = \left( \frac{C^*}{C^*_{\text{max}}} \right)^2$$

and equation for coefficient of fullness of combustion will be

$$\eta = \left[ \left( \frac{C^*}{C^*_{\text{max}}} \right)^2 - 1 \right] \quad (5.20)$$

Maximum value of characteristic speed  $C^*_{\text{max}}$  can be determined by knowing thermodynamic properties of gases formed during combustion of fuel; it corresponds to full transformation of components in products of combustion. If another value of  $C^*$  corresponds to the process with less fullness of combustion, then the ratio of  $C^*/C^*_{\text{max}}$  expresses the degree of burning of fuel.

In the presence of experimental method of determination of local temperature, speed and adiabatic coefficient, it may be easy to calculate coefficient of fullness of combustion and judge the kinetics of transformation of fuel in combustion chamber.

Coefficient of fullness of combustion can be presented as:

$$\eta = 1 - \frac{C}{C_0} \quad (5.21)$$

where  $C_0$  is initial concentration of one of the components.

whereupon

$$C_0 = \gamma \frac{1}{1+\alpha}$$

where  $\gamma$  — specific gravity of gas mixture;

$n = \frac{G_f}{G_0}$  — ratio of second expenditures of fuel and oxidant;

$C$  is average concentration of component, equal to final concentration of it in products of combustion.

Speed of diffusion burning  $v_d$  one can determine as the quotient from division of concentration  $C$  by time of turbulent burning:

$$v_d = \frac{C}{\tau_d} = C_0 \frac{1-\xi}{\tau_d}. \quad (5.22)$$

During the absence of linear agitation, which, obviously, more than ever matches uniflow chamber, and, therefore, the isolated burning of a fuel mixture, the speed of burning  $v_f$  can be determined as the derivative of concentration in time

$$v_f = \frac{dC}{d\tau_d} \quad (5.23)$$

or

$$v_f = C_0 \frac{d\xi}{d\tau_d}. \quad (5.24)$$

Equating (5.22) and (5.24), we have

$$\frac{d\xi}{d\tau_d} = 1 - \xi \quad (5.25)$$

and

$$\xi = 1 - e^{-\tau_d/\tau_{ns}}, \quad (5.26)$$

where

$$\tau_{ns} = \frac{\tau_n}{\gamma_d}.$$

Equating expressions (5.20) and (5.26), we receive equation of stationary method

$$\frac{1}{n} \left[ \left( \frac{C^*}{C_0} \right)^2 - 1 \right] = 1 - e^{-\tau_d/\tau_{ns}}. \quad (5.27)$$

At  $\tau_{ns} = \text{const}$ , the ratio of pressure to expenditure also remains constant.

Changes of time of turbulent burning leads to disturbance of stability of working process, pressure in chamber ceases to correspond to weight expenditure of fuel and oscillations appear.

According to the presented formula it is possible to calculate influence of different parameters on stability of process. As will be shown below, in hydrodynamic theory of stability for description of process in chamber we also use total time characteristic — time of conversion of fuel, or in the consideration of propulsion system of liquid-fuel rocket engine — time lag.

On boundary of stability of system of liquid-fuel rocket engine according to hydrodynamic theory, time of conversion changes and there appears non-stationary conditions. Thus, on the one hand, time of turbulent burning, having principal value in diffusion theory, opens more deeply the physicochemical nature of the time characteristics of the hydrodynamic theory of stability, and on the other hand, in the use of methods of this theory it is possible to explain influence of different parameters of propulsion system for time of turbulent burning.

Large value for understanding of stationary process of burning in liquid-fuel rocket engine and its stability have works connected with analysis of conditions of movement in cylindrical combustion chamber in the case when release of heat occurs in an insignificant section of it [117], [118], [119].

Release of heat in a small section of combustion chamber leads to appearance in the flow of a thermal jump. If zone of burning in chamber is considered as a region of thermal jump, then it is possible to apply for description of working process in liquid-fuel rocket engine, the main relationships of the hydrodynamic theory of burning and detonation.

Recently, Troshin [120] showed that in the mentioned idealization, real modes of burning in their thermodynamic and gas-dynamic characteristics are described as the lower branch of the adiabatic line of Hugoniot. Lower branch of adiabatic line of Hugoniot embraces modes of burning with speeds from  $u_n$  to maximum speed, corresponding to thermal crisis, i.e., speed of burning equal to speed of sound.

Description of conditions of burning in chamber of liquid-fuel rocket engine by lower branch of curve of Hugoniot allows in the first approximation to conduct

comparative appraisal of main parameters of engine, judge the degree of forcing of the mode of burning and analyze stability of working process of the engine.

Received equations can be used for tentative calculations and generalizations of experimental results. Further researches of process of burning should uncover nature of magnitude of time of turbulent burning, and also those factors, upon which it depends.

## Section 2. Experimental Investigations

Published researches in the area of study of stationary process of burning in chamber do not carry a systematic character and in them it is difficult to determine development of any main direction.

Above it was shown that degree of fullness of transformation of fuel and speed of its combustion can be easily calculated, if we measure temperature, speed, average molecular weight and ratio of thermal capacity of products of burning. Such measurements give the possibility to study kinetics of transformation of fuel and structure of zone of burning, and consequently, to determine volume of combustion chamber required for burning of fuel depending upon nature of fuel and design of engine [121], [122].

The pattern of increase of temperature of gas and kinetics of process from injector nozzles along axis of engine with thrust 454 kg during work on fuel (nitric acid + hydrocarbon) was explained in [121]:

According to received results, the temperature above all changes in a section located at a distance of 95—120 mm from the plane of the nose. These changes become all the less noticeable during further displacement downwards along the flow. Speed of products of burning also continuously increases by measure of movement of them from spray burner to nozzle. In all cross sections, changes of speed in radial direction are very small.

Consecutive transformation of fuel at given temperature, i.e., change of

chemical composition of gases by measure of removal from nose of engine to nozzle, can give an image of chemical transformations in corresponding temperature fields.

In Table 14 is listed the typical composition of products of burning of a sample taken near the input into nozzle.

Table 14. Composition of Gas Sample, Taken from Combustion Chamber of Rocket Engine Near Input to Nozzle (Fuel: Nitric acid + Hydrocarbon) [121]

(a) Состав продуктов горения	(b) Molar fraction
(b) Двухкись углерода (CO <sub>2</sub> )	0,221
(c) Окись углерода (CO)	0,008
(d) Вода (H <sub>2</sub> O)	0,111
(e) Водород (H <sub>2</sub> )	0,003
(f) Двухкись азота (NO <sub>2</sub> )	0,000
(g) Окись азота (NO)	0,008
(h) Азот (N <sub>2</sub> )	0,163
(i) Кислород (O <sub>2</sub> )	0,001
(j) Газообразные углеводороды	0,002

KEY: (a) Composition of products of burning; (b) Carbon dioxide (CO<sub>2</sub>); (c) Carbon monoxide (CO); (d) Water (H<sub>2</sub>O); (e) Hydrogen (H<sub>2</sub>); (f) Nitrogen peroxide (NO<sub>2</sub>); (g) Nitrogen oxide (NO); (h) Nitrogen (N<sub>2</sub>); (i) Oxygen (O<sub>2</sub>); (j) Gas hydrocarbons; (k) Molar fraction.

Change of chemical composition of gas by measure of removal from head of engine can give certain information concerning flow of process. From Fig. 48 it is clear that molar fractions of nitrogen oxide and oxygen very sharply fall by measure of advance of gases to nozzle, the biggest decrease with this occurs in zone between 95 and 120 mm from head of engine. This zone is, as it were, the boundary of the wide front of the flame. On the other hand, concentration of nitrogen increases with decrease of concentration of nitrogen oxide, indicating that the molecular nitrogen in products of burning will be formed from nitrogen oxide. This is in accordance with researches of Zel'dovich and Shaulov [47], Nasirov and Shaulov [48] concerning the two-stage mechanism of burning of mixtures containing NO<sub>2</sub>.

Connection between oxide of nitrogen and nitrogen forces us to assume that ratio of concentrations of nitrogen oxide and nitrogen can be useful criteria for

judgment concerning character of flow of processes of burning. Small value of ratio of  $\text{NO}/\text{N}_2$  indicates presence of great concentration of nitrogen and, consequently, the large fullness of reaction and vice versa.

In quoted work it was shown that at a distance of 95 mm from spray burner, the ratio of nitrogen oxide to nitrogen will attain maximum value, and temperature — minimum value. Good conformity between  $\text{NO}/\text{N}_2$  and temperature of gas is still not an indication that among these two parameters there exists a direct connection, conversely, the curve of dependence of  $\text{NO}/\text{N}_2$  on temperature has a quite complicated character. However, the presence of such connection indicates that the process of decomposition of  $\text{NO}_2$  carries a phasic character and nitrogen occurs as a result of thermal dissociation of  $\text{NO}$ .

Influence of design of engine on process of combustion, character of transformation of fuel along axis of engine and duration of this transformation are in great dependence on the design of injector nozzles of head of engine. Tests of injector nozzles of different design showed that characteristic speed ( $C^*$ ), determining fullness of transformation of fuel, strongly depends on structural peculiarities of the engine. Comparison of volumes of combustion chamber, required for obtaining the characteristic speed of expiration of determined magnitude, shows that for injector nozzles of one type is required  $515 \text{ cm}^3$ , but for injector nozzles of another type  $2380 \text{ cm}^3$ .

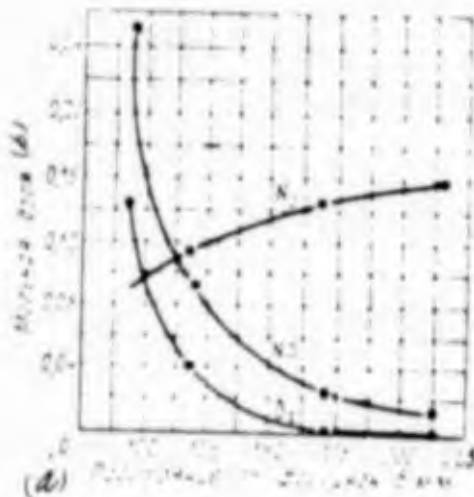


Fig. 48. Change of chemical composition of gas along length of chamber [121].  
KEY: (a) Distance from injector nozzles in mm; (b) Molar fraction.



Influence of type of injector nozzles on operating characteristics of engine is seen also from Fig. 49.

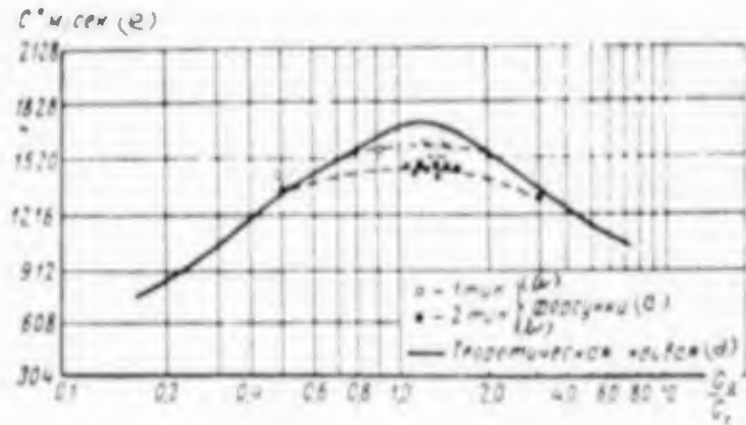


Fig. 49. Influence of type of injector nozzles on operating characteristics of engine [122].

KEY: (a) 1st type; (b) 2nd type; (c) After burners; (d) Theoretical curve; (e)  $C^*_{sp}$ /sec.

Comparison of work of two combustion chambers, identical in dimension, but distinguished by design of head of engine, i.e., number and location of injector nozzles, was conducted by Vulis [106].

Comparison of experimental and calculated characteristics based on a large number of experiments, shows that time of combustion for chamber No. 1 will be greater than for chamber No. 2, and, consequently, fullness of combustion and specific thrust during identical expenditure of fuel will be lower (Fig. 50, 51, 52). As a result of analysis it is possible to establish that the only cause decreasing fullness of combustion is sharp impairment of turbulent mixing.

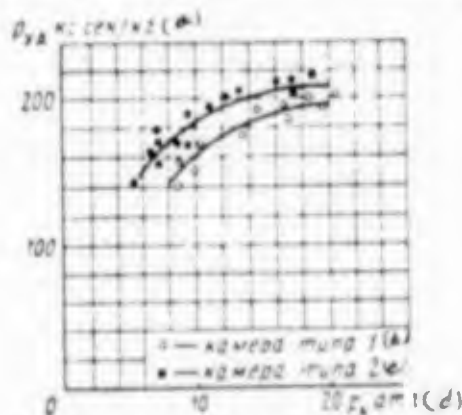


Fig. 50. Relation of specific thrust to pressure in chamber [106].

KEY: (a)  $P_{sp}$  kg sec/kg; (b) Chamber of type 1; (c) Chamber of type 2; (d)  $P_k$  atm(abs.).

With the help of the diffusion theory of burning in this work was explained the influence atomization on fullness of combustion, and processing of experimental data is essentially the first attempt of application, to design of engine, of presentations, well developed by the theory of diffusion burning.

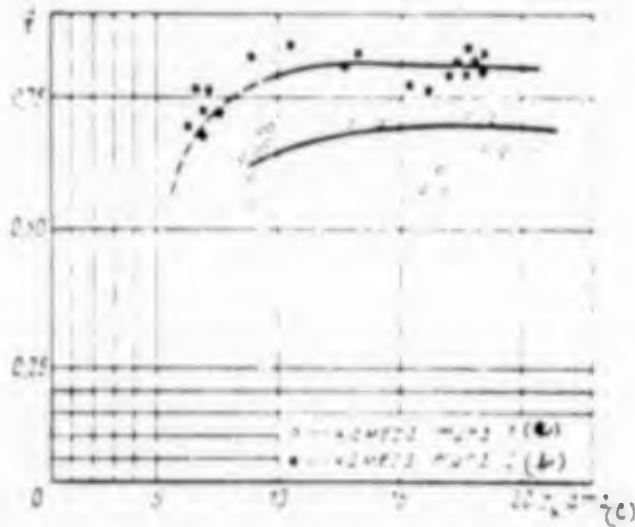


Fig. 51. Relation of completeness of combustion to pressure in chamber [106].  
KEY: (a) Chamber of type 1; (b) Chamber of type 2; (c) atm(abs.).

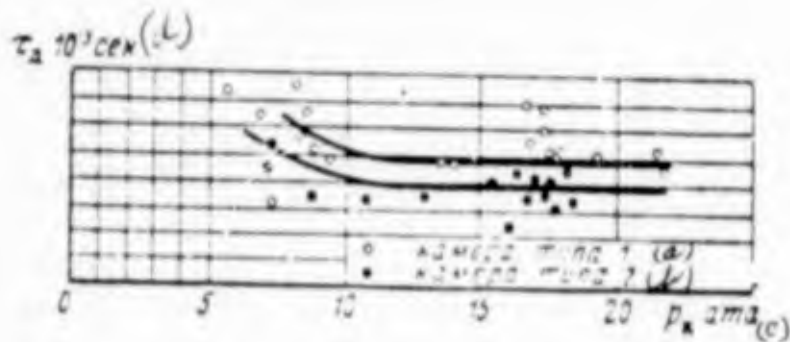


Fig. 52. Relation of time of turbulent burning to pressure in chamber [106].  
KEY: (a) Chamber of type 1; (b) Chamber of type 2; (c) atm(abs.).  
(d) sec

## CHAPTER VI

### INSTABILITY OF COMBUSTION PROCESS

Among researches in the area of combustion processes in technology, those connected with stability of operation process in motors turned out to be most urgent.

Effect of instability of combustion process on performance of motor can be most diversified. In certain cases there appear vibrations in controls, as well as mechanical and thermal failures of motors. In connection with this, efforts of researchers of various specialties in studying causes of appearance of combustion instability and searching for ways of its elimination are understandable.

Liquid propellant jet power plant, including also the engine, is a dynamic system. Contemporary theory of stability of dynamic systems, regardless of the form of its statement, is based on Lyapunov's research in stability of motion.

In his doctoral dissertation "General Problem in Motion Stability" (1892), Lyapunov advanced a direct method for investigation of stability of nonlinear systems ("second method") and proved theorems of validity of research in first order of approximation.

Lyapunov for the first time determined with mathematical precision the concepts of stability, serving as a basis for solution of various problem, related to stability of movement and equilibrium of dynamic systems. Therefore, in giving an account of researches in the area of stability of working process in liquid-fuel

rocket engines, we considered it necessary to bring accurate definitions of main concepts of stability in the form as they were established by Lyapunov [123], [124], [125].

Let the dynamic system be described by differential equations in form

$$\frac{dq_i}{dt} = Q_i(t, q_1, q_2, \dots, q_k, \dot{q}_1, \dot{q}_2, \dots, \dot{q}_k) \quad (6.1)$$

(i = 1, 2, \dots, k).

where  $q_1, \dots, q_k, \dot{q}_1, \dots, \dot{q}_k$  — independent variables, determining position and speeds of system;

$Q_i$  — known functions of these variables.

Definite states of system correspond to various sets of initial values of quantities

$$q_1, \dot{q}_1, q_2, \dot{q}_2, \dots, q_k, \dot{q}_k \quad (6.2)$$

Let us consider particular solution, corresponding to selected system of initial values that we shall designate with the same letters, but with a line above:

$$\bar{q}_1, \dot{\bar{q}}_1, \bar{q}_2, \dot{\bar{q}}_2, \dots, \bar{q}_k, \dot{\bar{q}}_k \quad (6.3)$$

Particular solution of (6.1) in this case will be

$$q_i = f_i(t); \quad q_1 = f_1(t), \dots, q_k = f_k(t) \quad (6.4)$$

According to Lyapunov's terminology, this form of movement is called undisturbed, while all the other forms of movement will be called disturbed.

Let us consider solutions of system (6.2) whose initial conditions are close to initial conditions (6.3) of the given particular solution (6.4):

$$q_i = \bar{q}_i + \epsilon_i, \quad \dot{q}_i = \dot{\bar{q}}_i + \epsilon_i, \quad \dots, \quad q_k = \bar{q}_k + \epsilon_k, \quad \dot{q}_k = \dot{\bar{q}}_k + \epsilon_k \quad (6.5)$$

Constants  $\epsilon_1$  and  $\epsilon_2$  are small in absolute value and are called disturbances. Assignment of constants  $\epsilon$  determines fully the disturbed movement.

Let us consider for undisturbed movement certain continuous functions  $Q_1, \dots, Q_n$  of quantities  $q_1$  and  $\dot{q}_1$  and time  $t$ , embracing every possible value of  $q_1$  and  $\dot{q}_1$ . For undisturbed movement, functions  $Q_i$  after replacement (6.4) will

change into some known functions of  $t$  that we shall designate through  $F_s$ , and for disturbed movement, according to the formula (6.5), they will be certain functions of  $t$  and disturbances  $\epsilon$ .

At  $t_1$  and  $t_1 = 0$ , difference  $Q_s - F_s$  will be equal to zero at any  $t$ . If, however,  $t_1$  and  $t_1$  are not equal to zero, then arises the following question: is it possible to expect that absolute values of differences  $Q_s - F_s$  will remain small for all values of  $t > t_0$ .

It is obvious that the answer depends on the character of undisturbed motion and on selection of function  $Q$ . If  $Q_s - Q_f$  for all values of  $t > t_0$  are very small, then it is possible to assert that the undisturbed movement is stable in relation to quantities  $Q_s$ , and the movement will be unstable, if only one of these quantities will not remain very small in the interval  $t > t_0$ .

We shall present definition of stability by Lyapunov.

If to any system of randomly given, arbitrarily small positive numbers  $L_1, L_2, \dots, L_k$  corresponds such a system of positive numbers  $E_1, E_2, \dots, E_k, \epsilon_1, \dots, \epsilon_k$ , then inequalities

$$|q_i| \leq E_i, \quad |f_i| \leq \epsilon_i \quad (6.6)$$

and, at any value of  $t > t_0$ , are satisfied inequalities

$$|Q_s - F_s| < L_s \quad (6.7)$$

then the undisturbed movement is called stable in relation to quantities  $Q_s$ ; otherwise, the undisturbed movement is called unstable.

If, having observed conditions (6.6) and (6.7), we have, apart from that,

$$\lim_{t \rightarrow \infty} |q_i - f_i(t)| = 0 \quad (6.8)$$

then the disturbed movement is sufficiently close to undisturbed one and approaches it asymptotically.

Thus, the solution of question about stability of the given undisturbed movement with respect to quantities  $Q_s$  is reduced to investigation of possibilities of finding such limits  $L_s$  that do not exceed the value of differences  $Q_s - F_s$ .

Theory of stability of movement has a sufficient number of methods for solution of such a problem and difficulties arising during investigation of stability of the dynamic system of liquid-fuel rocket engine are explained by the difficulty of composing differential equations of individual sections of this system.

Recently, in a series of works was described experimental material on unstable burning in chambers of liquid-fuel rocket engine [126] -- [131]. There were developed quantitative theories, explaining causes of appearance of two main forms of oscillations, low-frequency oscillations with frequency 15-600 cps and high-frequency oscillations with frequency over 600 cps [132] -- [138].

Low frequency oscillations appear as a result of causes that are determined by characteristics of the feed system, or as a result of "intra-chamber" instability. The latter form of low frequency oscillations does not depend on the feed system and, as was asserted by certain researchers [134], it appears as a result of the fact that the rate of burning depends on pressure and temperature in combustion chamber.

High frequency oscillations appear due to heterogeneity of physical conditions in definite places of combustion chamber.

If at low frequency oscillations one can disregard time of wave propagation, and the sole condition determining appearance of this form of instability is the time condition, then in the case of high frequency oscillations the time of propagation of pressure wave becomes commensurable with the period of oscillations and cannot be ignored.

The very best conditions for excitation of the system will be created in the case when frequency of wave propagation is close to one of natural frequencies of oscillations of gases in combustion chamber.

Chief characteristic of this form of oscillations consists in the fact that during concentration of combustion process near loops of the wave (maximum pressure) there are observed significant deviations of burning speeds and the greatest



tendency to instability of the system. Researches in the area of instability explained a number of phenomena, observed during the appearance of oscillations in combustion chamber, and indicated ways for their elimination.

Researches published in periodic literature can be divided into three groups [139].

The first group includes researches in which by means of the method of small disturbances is analyzed the stability of plane front of flame, i.e., instead of investigations of turbulent flames, in which the disturbance of flow has a very complicated nature, there is conducted an analysis of influence of periodic or continuous disturbances on stationary front of flame in laminar flow. Although such researches are still insufficient in examination of stability of the working process in motors, they are nevertheless of interest from the view point of the formulation of problem, <sup>its/</sup> solution and conclusions. The problem of whether the burning is stable or unstable in case of flame propagation along a motionless gas mixture, or in laminar flow, was considered in works [34], [36]-[38], [43]-[45].

If the width of combustion zone is small by comparison with characteristic dimensions of a vessel where the chemical reaction occurs, a purely gas-dynamic problem becomes separable from chemical problem. Therefore, disregarding the thickness of combustion zone, one can consider the stability of interface of combustion products in fresh mixture.

As a result of these researches [34], it was shown that the front of flame is absolutely unstable. This paradoxical conclusion became a subject of researches.

Study of structure of flame front as well as taking into account viscosity of medium and curvature of flame front, contributed nothing essentially new. One thing is obvious; even an "elementary" front of flame is unstable and may serve as a generator of disturbances also during the construction of a model of more complicated phenomena, for example burning, in a motor. This circumstance must be taken into account.

The second group of researches include those where conditions of progress of complicated chemical reactions are considered as main causes of disturbance of stability.

There exists a number of experimental facts, showing that chemical reactions in a certain range of variables lead to stabilization of natural-oscillation process.

In works of Frank-Kamenetskiy, Salnikov, et al. [46], [116] were proposed special kinetic diagrams of the progress of two consecutive reactions with the various temperature dependence. These researches showed that such a two-stage mechanism of reaction causes the process to assume periodic character.

There are distinguished basically oscillations of two forms: purely kinetic oscillations, connected only with change in concentration of intermediate products of reaction, and thermokinetic oscillations, connected simultaneously with both the kinetics of reaction, and with the liberation and dissipation of heat. Besides kinetic and thermokinetic oscillations, there are possible also relaxation oscillations, appearing in dependence on the rate of fuel mixture feed into combustion chambers.

A group of works, where physicochemical processes in motor are analyzed with the help of over-all time parameters, are of interest from this viewpoint.

Burning of fuel mixture in chamber, for example, according to Vulis [115] can be conceived of as a result of "competition" of two opposite phenomena: on the one hand, there occurs turbulent mixing and burning of components, and, on the other hand, products of combustion depart from the chamber under the influence of higher pressure.

At those temperatures that take place in a motor, time of turbulent mixing and burning of components are determined basically by the speed of mixture preparation and intensity of turbulent interchange of gases.

The time of turbulent mixing is determined by two main factors — primary splitting of components entering the chamber and by the character of subsequent

mixing:

$$\tau = \frac{d_p}{D_t}$$

Numerator of this fraction is determined by average dimension of fuel particle, and denominator can be calculated, for example, by the well-known approximated Damköhler's formula for turbulent diffusion.

Analysis of the progress of working process shows that main gas-dynamic parameters of motor: temperature, speed and, mainly, time of stay remain constant as long as there exists a linear connection between pressure in chamber and total consumption. When operating conditions of the motor change, all these quantities begin to change.

The time of turbulent burning remains constant, since a change of this time would cause a decrease in completeness of combustion and, consequently, disturbance of linearity. Deviation of pressure increase from the law of proportionality to consumption is explained by change in time of turbulent burning.

Thus the process of burning in chamber in case of its steady state should be confined within a definite time, viz., time of turbulent burning. A similar viewpoint has expressed recently by Karman [180].

In a number of works, qualitative and quantitative researches in the area of stability were executed successfully by introduction of time parameter.

In these researches, time from the moment of injection to transformation of fuel mixture into products of combustion, (called time of conversion or time lag  $\tau$ ) is the principal kinetic characteristic of combustion process in the chamber of liquid-fuel rocket engines.

Since the introduction of quantity  $\tau$  allowed to obtain rather valuable results, we shall conduct later on a detailed analysis of dynamic stability of the system, using this parameter.

One can assume that accumulation of physicochemical researches concerning the chamber of liquid-fuel rocket engine will evidently introduce clarity into mechanism

of burning and, in view of this fact, our concepts of causes disturbing the stability of working process in liquid-fuel rocket engine will be significantly improved.

### Section 1. Analysis of Low-Frequency Instability

As was shown in Chapter V, the actual processes, occurring in a combustion chamber, present large difficulties for quantitative analysis. However, if we make a series of simplifying assumptions, then it is easy to create a working model for analytic investigations.

The following are the main assumptions:

1. A definite time identical for all particles of fuel is required for transformation of fuel into products of combustion. The presence of such time — time of conversion — leads to the fact that the processes in the combustion chamber lag as compared to the processes in pipe lines.

2. Study of the process of burning atomized fuel shows that at high temperatures and great reaction ability of fuel components the stationary method is determined mainly by the hydrodynamic properties of the system [53], [116].

This form of burning according to existing terminology is called diffusion burning.

The process of regulating diffusion burning is reduced to regulating fuel atomization [140]. In such a placement of the question the application of the main positions of the theory of regulation has a special significance in the process of burning in liquid-fuel rocket engines.

An analysis of the principle of work of liquid-fuel rocket engines with gas tank feed shows that the combustion chamber of the propulsion system can be considered as an object of regulation and the process of entering the components and their conversion into gaseous products of reaction are regulators of the object. Operating conditions of the engine are automatically supported by a system of feeding. However the solution of various problems combined with regulation and forcing of

liquid-fuel rocket engines shows that the presentation concerning a system of liquid-fuel rocket engines, as concerning the system of automatic regulation, can be applicable to methods of burning, occurring in the diffusion area. The remaining methods are unregulated and usually lead to damages to the propulsion system.

A similar analogy was introduced in work [136], in order to show the possibility of stabilization of a system outside of the dependence on the magnitude of time of conversion, and in work [135] — for investigation of the stability of the process of burning.

Examination of the dynamic system of liquid-fuel rocket engines as systems of automatic regulations permits the identification of the time of conversion with conventional time lag in the theory of adjustment.

3. Pressure in the combustion chamber is practically equal throughout the entire chamber in every moment of time and the mass of gases in it fluctuates near the mean value as one whole.

4. Temperature of gas in the chamber is constant and even and does not depend on fluctuations of pressure.

For an investigation of the stability of a system with gas cylinder feed it is necessary to compose differential equations of its separate sections.

The following are equations of these sections:

- 1) equations of the motion of gas flow in the combustion chamber;
- 2) equations of the flow of liquid through pipe lines.

Equations of sections in totality describe the dynamic state of the propulsion system.

#### 1. Equation of the Combustion Chamber

Burning of fuel mixture in combustion chamber is composed of chemical and gas-dynamic processes, therefore such an equation should include equations of motion of gas mixture and equations of chemical kinetics.



Gas flow in combustion chamber is considered as flow of gas, which is determined by laws of conservation of mass, momentum and energy.

Simplifications resulting from the assumptions (see pages 1 and 2), completely replace the equation of the amount of motion and insert the equation of energy. In the presence the following assumption (see page 2) it is not necessary to know the character of burning in volume. And finally, if time of lag is constant, then it is possible also disregard the distribution of burning in time.

On the basis of these assumptions the dynamics of the gas flow in combustion chamber in essence is described as the equation of mass balance.

The combustion chamber in this case can be represented as a consecutive formation of a lagging section where processes of conversion of fuel and single capacity section take place [141], [142], [143].

Such a presentation concerning the combustion chamber allows the possibility of writing a differential equation of the combustion chamber taking into account the pre-flame processes [128], [129].

Using the first assumption we can write that the quantity of the formed products of combustion in a moment of time  $t$  is equal to the quantity of injected fuel during the time  $t - \tau$ :

$$G_p(t) = G_f(t - \tau) \quad (6.9)$$

The quantity of gases in the combustion chamber is determined from an equation of the state

$$G_g = \frac{p V}{RT_g}$$

If we allow that a small deviation of pressure from the stationary value occurs at constant temperature, the speed of build-up of pressure will be

$$\frac{dG_g}{dt} = \frac{V}{RT_g} \frac{dp}{dt} \quad (6.10)$$

The quantity of fuel, proceeding in the combustion chamber during the time  $dt$ , should be equal to the available quantity of gases in <sup>a/</sup>considered moment of time plus the quantity of gases, exiting from the chamber:

$$G_f(t - \tau) dt = dG_g + G_g dt \quad (6.11)$$



where

$$U_n = \sqrt{\frac{kR}{k+1} \left( \frac{c}{a} \right)^{2k+1} P_n F_{sp}}$$

or

$$U_n = \frac{F_{sp} F_{sp} c}{C^*}$$

In the equation (6.11) let us place an expression for  $dG_k$  and  $G_n$  then the equation of the combustion chamber takes on the following form:

$$G_{\Phi}^2 (t-t_0) = \frac{F_{sp} F_{sp} c}{C^*} - \frac{v_{sp}}{RT_n} \frac{dP_n}{dt} \quad (6.12)$$

or

$$K_1 (G_{\Phi}^2 (t-t_0) - P_n) = \frac{v_{sp}}{RT_n} \frac{dP_n}{dt} \quad (6.13)$$

where

$$K_1 = \frac{C^*}{F_{sp} R} \text{ and } \tau_n = \frac{v_{sp} C^*}{RT_n F_{sp} R}$$

## 2. Equation of Motion of Components Along Pipe Lines

The two-component system of liquid-fuel rocket engines, besides the combustion chamber, still has in its composition two parallel connected pipe lines. Introduction of a second main line changes the character of the boundary of stability, and together with this the dependence of time of delay on the constructive parameters of system changes also. Introduction of a second main line leads to the fact that the system as a result of mutual influence of movement of components along main line obtains new dynamic qualities.

For conclusion of equation of motion of components, which are identical for fuel and oxidizer, we will use an equation of energy balance, with this compressibility of liquid, elasticity of pipe lines, and also forces of inertia in spray burners will be disregarded [135].

The work, accomplished by the liquid during its motion from the tank in the combustion chamber during the time  $dt$ , is expended in the change of the kinetic

energy of the liquid between the spray burners and the tank, in loss of energy due to the presence of forces of inertia of a mass of liquid, and also in losses due to friction.

In this case an equation of motion of fuel through the pipe line can be presented in the following form:

$$\begin{aligned} & (p_0^r F_0^r v_0^r - p_n F_\Phi^r v_\Phi^r) dt - \left( \frac{G_r}{2g} (v_0^r) - \frac{G_r}{2g} v_{\Gamma p}^r \right) dt + \\ & \frac{\gamma_r}{g} l_{\Gamma p}^r F_{\Gamma p}^r v_{\Gamma p}^r dv_{\Gamma p}^r + f_r \frac{l_r}{d_r} \frac{G_r}{g} (v_{\Gamma p}^r)^2 dt. \end{aligned} \quad (6.14)$$

For simplification of the equation (6.14) we use an equation of inseparability, preliminarily dividing into  $F_{\Gamma p}^r V_{\Gamma p}^r dt$

$$F_0^r v_0^r = F_{\Gamma p}^r v_{\Gamma p}^r = v_\Phi^r F_\Phi^r. \quad (6.15)$$

The Equation (6.14) will be copied as:

$$\begin{aligned} p_0^r - p_n &= \frac{G_r}{2g} v_\Phi^r \frac{1}{F_{\Gamma p}^r v_{\Gamma p}^r} - \frac{G_r}{2g} v_0^r \frac{1}{F_{\Gamma p}^r v_{\Gamma p}^r} + \\ & + \frac{\gamma_r}{g} l_{\Gamma p}^r \frac{dv_{\Gamma p}^r}{dt} + f_r \frac{G_r}{g} \frac{l_r}{d_r} \frac{v_{\Gamma p}^r}{F_{\Gamma p}^r}. \end{aligned} \quad (6.16)$$

We will substitute from the equation (6.15) the values  $v_\Phi^r$  and  $v_0^r$  in equation (6.16), then

$$\begin{aligned} p_0^r - p_n &= \frac{G_r}{2g} \frac{F_{\Gamma p}^r v_{\Gamma p}^r}{(F_\Phi^r)^2} - \frac{G_r}{2g} \frac{F_{\Gamma p}^r}{(F_0^r)^2} v_{\Gamma p}^r + \\ & + \frac{\gamma_r}{g} l_{\Gamma p}^r \frac{dv_{\Gamma p}^r}{dt} + f_r \frac{G_r}{g} \frac{l_r}{d_r} \frac{v_{\Gamma p}^r}{F_{\Gamma p}^r}. \end{aligned} \quad (6.17)$$

Equation (6.17) can be simplified, if instead of speed we substitute its expression from the equality

$$\begin{aligned} G_r &= \gamma_r v_{\Gamma p}^r F_{\Gamma p}^r; \\ p_0^r - p_n &= \frac{G_r^2}{2g \gamma_r F_\Phi^r} \left[ 1 - \left( \frac{F_\Phi^r}{F_0^r} \right)^2 + 2f_r \left( \frac{F_\Phi^r}{F_{\Gamma p}^r} \right) \frac{l_{\Gamma p}^r}{d_{\Gamma p}^r} \right] + \\ & + \frac{1}{g} \frac{l_{\Gamma p}^r}{F_{\Gamma p}^r} \frac{dG_r}{dt}. \end{aligned} \quad (6.18)$$

Finally we will receive

$$p_0^r - p_n = \beta_i G_i^2 + \beta_i^* \frac{dG_r}{dt}. \quad (6.19)$$

where

$$\beta_i = \left[ 1 - \left( \frac{F_\Phi^r}{F_0^r} \right)^2 + 2f_r \left( \frac{F_\Phi^r}{F_{\Gamma p}^r} \right) \frac{l_{\Gamma p}^r}{d_{\Gamma p}^r} \right] \frac{1}{2g \gamma_r} F_\Phi^r$$

and

$$\frac{\partial p_r}{\partial t} = \frac{1}{K} \frac{dG_r}{dt}$$

In/similar way it is possible to show that the equation of motion for the oxidizer will be

$$p_0'' - p_0 = \frac{1}{K} G_0 + \frac{1}{K} \frac{dG_0}{dt} \quad (6.20)$$

We will apply to equations (6.19) and (6.20) the method of regular linearization [141], [142], [143], allowing dissociation of the nonlinear function of several variables in Taylor series in degrees of small deviations, taken near their values, corresponding to established method.

Then equations (6.19) and (6.20) will be copied in the form of

$$\Delta p_r = \frac{\partial \Delta p_r}{\partial G_r} G_r + \frac{1}{K} \frac{dG_r}{dt} \quad (6.21)$$

or

$$K_1 \Delta p_r = G_r + \theta_r \frac{dG_r}{dt} \quad (6.22)$$

where

$$K_1 = \frac{G_r}{\Delta p_r} \text{ and } \theta_r = \frac{G_r \tau_r}{2K \Delta p_r} \quad (6.23)$$

For the oxidizer

$$\Delta p_0 = \frac{\partial \Delta p_0}{\partial G_0} G_0 + \frac{1}{K} \frac{dG_0}{dt} \quad (6.24)$$

or

$$K_2 \Delta p_0 = G_0 + \theta_0 \frac{dG_0}{dt} \quad (6.25)$$

where

$$K_2 = \frac{G_0}{\Delta p_0} \text{ and } \theta_0 = \frac{G_0 \tau_0}{2K \Delta p_0} \quad (6.26)$$

In differential equations (6.13), (6.22) and (6.25) the system we enter a series of coefficients, having a definite physical meaning. It is easy to show that coefficients  $\tau_r, \theta_r$  and  $\tau_0$  have dimension of time, but  $K_1, K_2$  and  $K_3$  are dimensionless parameters.

A problem of further research is the ascertaining of the role of separate parameters in the determination of the conditions, necessary and sufficient so that the

system, described by equations (6.13), (6.22) and (6.25), was stable.

We will write these equations in the form of operators

$$\left. \begin{aligned} p_n(\tau_n p + 1) &= K_1 G_1 e^{-\tau_n p} \\ G_r(\theta_r p + 1) &= K_2 \Delta p_r \\ G_0(\theta_0 p + 1) &= K_3 \Delta p_0 \end{aligned} \right\} \quad (6.27)$$

where  $p$  — symbolic image of differentiation in operational form\*.

For solution of this problem it is necessary to obtain a characteristic equation of the system excluding from obtained differential equations (6.27) all variables besides pressure in combustion chamber.

We will use Cramer's rule [144] and will write determinant of system (6.27):

$$\Delta p_n = \begin{vmatrix} \tau_n p + 1 & -K_1 e^{-\tau_n p} & -K_1 e^{-\tau_n p} \\ K_2 & \theta_r p + 1 & 0 \\ K_3 & 0 & \theta_0 p + 1 \end{vmatrix} = 0.$$

We discover the determinant of the system and after conversions receive

$$ap^3 + bp^2 + c_p + K_0(\theta_r p + 1)e^{-\tau_n p} = 0, \quad (6.28)$$

where

$$a = \tau_n \theta_0 \theta_r; \quad b = \tau_n \theta_0 + \theta_r \theta_0 + \tau_n \theta_r;$$

$$c = \tau_n + \theta_0 + \theta_r; \quad \theta_r = \frac{1 + (\beta_r^* \beta_0^*)}{1 + n \frac{\Delta p_r}{\Delta p_0}}$$

or

$$\theta_r = \frac{K_2 \theta_0 + K_3 \theta_r}{K_2 + K_3} n \Delta K_0 = K_1 (K_2 + K_3).$$

### 3. Determination of Boundary of Stability

Analysis of stability of any dynamic system can be conducted or for the purpose of revealing of stability of concrete system, all parameters of which are given, or for the purpose of determination of all possible values of parameters, with which the system is stable.

Similar analyses are conducted with the help of criteria of stability, which determine the conditions, necessary and sufficient so that all roots of the characteristic equation of the system have a negative real part.

\*Operation of differentiation is possible conditionally to depict with the help of symbol  $p$ . Under its definite conditions it is possible to consider it as a number. This is easy to prove by means of application to differential equations of laplace transform [142].

In that case, when coefficients of characteristic equation are given and it is required to determine, whether or not the system is stable, we usually use the criteria of Routh, Hurwitz, Vyshnegradskiy, Mikhaylov-Nyquist or generalized criterion [145] — [150].

The equation (6.28) obtained for system with concentrated parameters is the most general. This equation can be simplified by means of dissociation of the exponential multiplier in a series with retention of first two members. Mathematical conversion of a similar kind was carried out in works [133], [134]. It is unlawful in case of construction of boundaries of stability, but inasmuch as it is applied in a number of investigations, we will show, how they are used.

Thus, equation (6.28) will be copied

$$ap^3 + (b - K_0 \theta_1 \tau) p^2 + (c + K_0 \theta_1 \tau - K_0 \tau) p + K_0 + 1 = 0 \quad (6.29)$$

This equation by means of dividing it into  $K_0 + 1$  and introduction of a new variable  $u$

$$u = \left[ \frac{a}{K_0 + 1} \right] p$$

leads to normalized form

$$u^3 + \frac{b - K_0 \theta_1 \tau}{a(K_0 + 1)} u^2 + \frac{c + K_0 \theta_1 \tau - K_0 \tau}{a(K_0 + 1)} u + 1 = 0 \quad (6.30)$$

or

$$u^3 + Au^2 + Bu + 1 = 0. \quad (6.31)$$

Boundary of stability of system, which is depicted by equation (6.31), is determined with the help of Vyshnegradskiy criterion

$$A \cdot B < 1. \quad (6.32)$$

On plane of parameters the equation will be depicted in the form of Vyshnegradskiy hyperbola determined by the expression

$$\frac{(b - K_0 \theta_1 \tau)(c + K_0 \theta_1 \tau - K_0 \tau)}{a(K_0 + 1)} < 1. \quad (6.33)$$

System will be stable, if  $A \cdot B > 1$  and unstable in case of  $A \cdot B < 1$ .

We will copy equation (6.33) in the form of the following inequality:

$$\frac{(b - K_0 \theta_1 \tau)(c + K_0 \theta_1 \tau - K_0 \tau)}{a(K_0 + 1)} < 1. \quad (6.34)$$

From inequality (6.34) it is easy to obtain Summerfield inequality [133], for that will be used values  $a$ ,  $b$  and  $c$  from equation (6.28), equating  $\theta_0$  or  $\theta_r$  and  $\theta_r$  with zero, we receive

$$\tau_n \theta_1 (\tau_n + \theta_r - K_0 \tau_n) = 0$$

and further

$$\frac{\tau_n + \theta_1}{K_0} = \tau_{sp}, \quad (6.35)$$

where  $\theta_1$  — temporary constant of main line.

We substitute values  $\tau_n$ ,  $\theta_1$  and  $K_0$  from equation (6.13), (6.23), (6.26), and (6.28), then

$$\frac{v_k}{RT_n G} 2\Delta p + \frac{G}{R} \frac{l_{sp}}{F_{sp} P_k} > \tau_{sp}$$

or in Summerfield designations [133]

$$\frac{L \cdot C \cdot 2\Delta p}{RT_n P_k} + \frac{l_{sp} \dot{m}}{P_k F_{sp}} > \tau_{sp}, \quad (6.36)$$

where

$$C^* = \frac{\sqrt{RRT_n}}{\Gamma \sqrt{k}}; \quad L^* = \frac{L_k F_k}{F_{sp}}; \quad \dot{m} = \frac{G}{R} \quad \text{and} \quad \Gamma = \left( \frac{2}{k+1} \right)^{\frac{k+1}{2(k-1)}}.$$

The characteristic equation of system (6.28) is transcendent. To analogous equations are reduced problems concerning stability of systems with delay, and also determination of dynamic properties of certain acoustic and radio-technical systems in the presence of lagging feedback.

Consideration of characteristic equation shows that determining parameters of stability of system are parameters  $\tau_n$ ,  $\theta_r$ ,  $\tau_1$ ,  $K_0$ .

Construction of boundary of stability in parameter spaces usually is done by method of D-subdivision [151], [152]. Such construction provides graphic presentation concerning boundary of stability of system.

Giving  $\omega$  different values from  $\omega=0$  to  $\omega=\infty$ , it is possible to calculate according to equations of value  $K_0$ ,  $\tau$  and along points to construct corresponding curves on plane  $K_0$  and  $\tau$  at constant values as  $\tau_n$ ,  $\theta_r$ ,  $\theta_0$  and  $\theta_r$ . Construction of D-subdivision in plane of three parameters is done in a similar way, whereupon the value of another parameter changes.



Qualitative examination of stability of single-component system is conducted in investigations [132], [133], and established besides that stability of system is characterized by two interconnected parameters: time of lag and ratio of fall of pressure to pressure in combustion chamber.

Increase of fall of pressure and decrease of time of delay leads to expansion of boundary of stability of system.

The hydrodynamic characteristics of the feed system have an essential value for expanding the boundaries of stability.

A more detailed qualitative examination of dynamic stability of a two-component system was conducted in work [135].

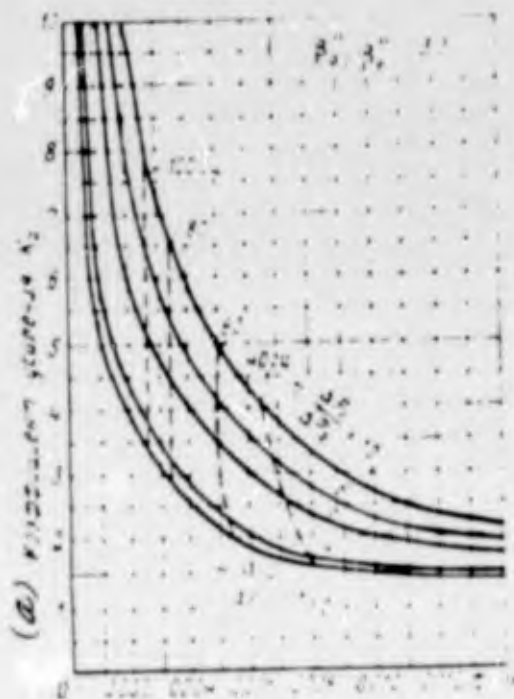


Fig. 53. Boundary of stability of system [135].  
KEY: (a) Strengthening coefficient.

In Fig. 53 are shown curves of boundaries of stability in coordinates  $K_0$  and  $\tau$ , where  $K_0$  is the amplification factor of the system, determined by the expression

$$K_0 = K_1(K_2 + K_3).$$

For their constructions the authors of this investigation used expansion in a number of multipliers  $e^{-\lambda t}$  of characteristic equation (6.28).

The zone, lying below every curve, represents an area of stable work of the system, and the zone, lying above curve, — an area of unstable work of the system.

From these curves it follows that with an increase of falls of pressure the stability of system increases at a given value of  $K_0$  or for a given time of delay are allowed higher values of  $K_0$ . The bigger the value of the ratio  $\frac{P_{1p}}{P_{1p}^0} \frac{F_{1p}}{F_{1p}^0} \frac{I_{1p}}{I_{1p}^0}$  the more extensive the area of stability.

How easy this is to note from Fig. 53 and 54, the time lag is not a physico-chemical constant, and depends on constructive and method parameters of the installation.

If the given system after checking it with the help of Mikhaylov-Nyquist criteria appears unstable, then by means of changing its parameters it is easy to suppress oscillation of low frequency in any band of frequencies.

## Section 2. "Intrachamber" Instability

Under intrachamber instability is understood such a form of oscillations of low frequencies, which appear in combustion chamber as a result of influence of physical factors (pressure, temperature) on process of burning. This form of oscillations of low frequency appears outside of dependence on the characteristics of the feeding system.

The stability of such a dynamic system was considered in a number of works. In published investigations [134], [138] the assumption was expressed that the total time lag is the sum of the constant and variable time of delay. Changes of the variable part of time of delay are combined with oscillations of pressure in the combustion chamber by a power function. The exponent in these works is called the index of interaction. Introduction of such a connection is founded on the fact that such processes, as atomizing or mixing, are the necessary preparatory phase for other processes, do not change under the influence of a change of pressure in combustion chamber. This position is controversial though because atomization of

fuel components is determined by the fall of pressure ( $p_0 - p_k$ ) and change of pressure in chamber immediately leads to changes of quality of atomization and the process of mixing also is not finished in the pre-flame zone and is continued in zone of burning. Consequently, such a division of time of delay is very conditional. Since this position found wide application in a number of works, then we will conduct further analysis of "intrachamber" instability using it.

The speed of the process of burning in combustion chamber is the function  $f(p, T)$  of pressure, temperature and any other physical factor. We designate through  $f(p, T)$  the quantity of heat, necessary for ignition of a unit of fuel mixture; if this quantity of heat is constant, then this can be recorded in the following form:

$$\int_{t_1}^{t_2} f(p, T, t) dt = \text{const.} \quad (6.37)$$

For a case of small disturbances it is possible to allow that at time delay ( $\tau$ ) affects only pressure and function  $f(p, T)$ , then  $p^n$  can be written in evident form, where  $n$  — index of interaction.

For composition of equation of balance of mass in combustion chamber we take, that the relative deviations of mass of gas, pressure and expenditure are equal to:

$$\frac{M - \bar{M}}{\bar{M}} = \frac{p - \bar{p}}{\bar{p}} = \frac{G - \bar{G}}{\bar{G}} = z(t) \quad (6.38)$$

If we take as earlier that  $\tau$  — time from moment of injection to transformation of fuel mixture into products of reaction, then the quantity of the substance, proceeding through the head between time

$$t - \tau \text{ and } t - \tau + d(t - \tau), \text{ is } G_{\Phi(t-\tau)} d(t - \tau),$$

and the equation of balance of mass

$$dM + G dt = G_{\Phi(t-\tau)} d(t - \tau) \quad (6.39)$$

or

$$\frac{dM}{dt} + G = G_{\Phi(t-\tau)} \frac{d(t - \tau)}{dt}$$

Equation (6.37) at constant temperature can be rewritten in the form

$$\int_{t_1}^{t_2} f(p(t')) dt' = \text{const.}$$

After differentiation in time we have

$$f[p(t)] - f[p(t-\tau)] \left(1 - \frac{d\tau}{dt}\right) = 0,$$

whereupon after expansion in Taylor series

$$f[p(t)] \approx f[p(t-\tau)];$$

or

$$\frac{d\tau}{dt} = \frac{p(t-\tau) - p(t) \frac{d \log f(p)}{d \log p}}{p} \quad (6.40)$$

where

$$\frac{d\tau}{dt} = n [\varphi(t-\tau) - \varphi(t)],$$

$$n = \frac{d \log f(p)}{d \log p}.$$

After introduction of time of stay of gases the equation of balance of mass in combustion chamber will be

$$\frac{1}{n} \frac{d\varphi}{dt} + \frac{1-n}{n} \varphi(t) - \varphi(t-\tau) = 0. \quad (6.41)$$

Characteristic equation of system for (6.41):

$$\frac{1}{n} S + \frac{1-n}{n} + e^{-s\tau} = 0. \quad (6.42)$$

Substituting  $s = \lambda + i\omega$  and dividing the active part from the imaginary part, we obtain

$$\left. \begin{aligned} \lambda + (1-n) + ne^{-\lambda\tau} \cos \omega\tau &= 0, \\ \omega - ne^{-\lambda\tau} \sin \omega\tau &= 0. \end{aligned} \right\} \quad (6.43)$$

At  $\lambda = 0$  critical values for frequency and time of delay

$$\omega^* = \sqrt{2n-1}$$

and

$$\tau^* = \frac{1}{\sqrt{2n-1}} \left[ \pi - \arctan \frac{\sqrt{2n-1}}{1-n} \right]. \quad (6.44)$$

Analysis of these equations shows that at  $n < 1/2$  the system is always stable independently of the value of the time of delay. Critical time lag always is decreased, when  $n \rightarrow 1/2$ . Increase of  $n$  leads to destabilization of the process, at  $n > 1$  the system is definitely unstable.

Calculations of index of interaction  $n$  from experimental values [153] shows that it is a significantly larger unit and increases with an increase of pressure in the combustion chamber.

### Section 3. Analysis of High-Frequency Instability

In Section 1 combustion chamber is considered as a regulated object, consisting of a lagging section and capacity, in which thermodynamic parameters are completely levelled in length and cross section. Strictly speaking, any real system is a system with distributed parameters. Replacement of them with concentrated parameters is a known kind of idealization, the legality of which depends on the width of the considered band of frequencies; as a rule, idealization loses correctness in the area of high frequencies.

In a general case the problem concerning the finding of conditions of stability of the working process in a combustion chamber is a spatial problem. Mathematically this signifies the solution of a three-dimensional problem, but in connection with the complexity of such an analysis and absence of sufficient experimental material for assignment of boundary conditions it is necessary to resort to significant simplifications.

It is allowed that all gas-dynamic and thermodynamic magnitudes are functions only of one coordinate and time. Motion of gas flow is depicted by equations of hydrodynamics, which after certain assumptions are reduced to usual equations of hydraulic shock. Consequently, calculation of distribution leads to calculation of wave phenomena, which are usually disregarded during investigations of low-frequency instability.

As during the analysis of low-frequency instability it is allowed that the front of the flame is located at the cut of the injector nozzles and burning is finished in a narrow zone. For transformation of fuel a definite time is required — a time lag.

It is further allowed that the process in the combustion chamber is isentropic and at small deviations of pressure from the established mode changes density a little. Speed of flow in combustion chamber is significantly slower than the speed of sound. These simplifications allowed accomplishment in works [134] and [136]



analysis of stability of combustion chamber for one-dimensional flow in case of the absence of pipe lines. Practically any propulsion system has in its own composition main lines for feeding components. Speeds of entering of components into combustion chamber are regulators of the process. When combustion chamber is the regulated volume with distributed parameters, it is extraordinarily important <sup>to</sup>/analyze the stability of the system in the presence of main lines.

A similar problem in the theory of regulation for the first time was considered by Kabakov [154] for the case of regulation of vapor pressure in a pipe line.

### 1. Differential Equations of Combustion Chamber

In a case, when the dynamic and thermodynamic magnitudes of flow are functions of one coordinate and time, Euler equations and equations of inseparability is reduced to a nonlinear system of the first order of differential equations in particular derivatives with three unknown functions  $v$ ,  $p$  and  $\rho$ :

$$\left. \begin{aligned} \frac{\partial v}{\partial t} + v \frac{\partial v}{\partial x} &= \frac{1}{\rho} \frac{\partial p}{\partial x} \\ \frac{\partial \rho}{\partial t} + \rho \frac{\partial v}{\partial x} + v \frac{\partial \rho}{\partial x} &= 0 \end{aligned} \right\} \quad (6.45)$$

In order to make the system definite, it is necessary to assign an equation of connection between  $p$  and  $\rho$  for isoentropy flow:

$$\left(\frac{\rho}{p}\right)^{\gamma} = \frac{f}{f'} \quad (6.46)$$

We replace in the equation (6.45) derivatives from density to derivatives from pressure according to

$$\frac{\partial \rho}{\partial t} \left(\frac{\partial \rho}{\partial p}\right) + \frac{\partial \rho}{\partial x} = \frac{1}{a^2} \frac{\partial p}{\partial t} \quad (6.47)$$

If we do not consider the resistance to movement of gas in combustion chamber  $\left(v \frac{\partial v}{\partial x}\right)$  and deviations of pressure in the process of the appearance disturbance  $\left(v \frac{\partial \rho}{\partial x}\right)$ , then from (6.45) we obtain

$$\left. \begin{aligned} \frac{\partial v}{\partial x} - \frac{1}{\rho a^2} \frac{\partial p}{\partial t} & \\ \frac{\partial v}{\partial t} - \frac{1}{\rho} \frac{\partial p}{\partial x} & \end{aligned} \right\} \quad (6.48)$$



We designate the relative deviation of pressure from its established value by  $\varphi$ , relative deviation of momentum of gas flow along combustion chamber by  $\psi$ , relative deviation of consumption by  $\xi$ , relative coordinate by  $\lambda$ :

$$\varphi = \frac{p - \bar{p}}{\bar{p}} = \frac{\Delta p}{\bar{p}}, \quad \psi = k \frac{v - \bar{v}}{\bar{v}} = k \frac{\Delta v}{\bar{v}}, \quad \xi = \frac{\Delta G}{G} \text{ and } \lambda = \frac{x}{L}. \quad (6.49)$$

Then equation (6.40) will be copies in the following form:

$$M^2 \tau_n \frac{\partial \psi}{\partial t} = - \frac{\partial \varphi}{\partial t}, \quad \tau_n \frac{\partial \varphi}{\partial t} = - \frac{\partial \psi}{\partial \lambda}, \quad (6.50)$$

where

$$\tau_n = \frac{L}{a}, \quad M = \frac{\bar{v}}{a}.$$

These equations are unknown equations for the combustion chamber in the case of one-dimensional flow, and they are equivalent to the ordinary wave equation. For solution to equations (6.50) we apply laplace transform [155]--[157], which will allow direction of the operation of solution of differential equations to simple operation of solution of algebraic equations.

We introduce images of functions

$$\varphi \rightarrow Z, \quad \psi \rightarrow W \text{ and } \xi \rightarrow \Sigma. \quad (6.51)$$

Equations (6.42) in images

$$M^2 \tau_n S (W - \psi_0) = \frac{dZ}{d\lambda}, \quad (6.51a)$$

$$\tau_n S (Z - \varphi_0) = \frac{dW}{d\lambda}. \quad (6.51b)$$

For solution of equations (6.51a) and (6.51b) we differentiate equation (6.51a) by  $\lambda$  and substitute  $dW/d\lambda$  from equation (51b), then

$$\frac{d^2 Z}{d\lambda^2} = M^2 \tau_n S \frac{dW}{d\lambda} = M^2 \tau_n S [\tau_n S (Z - \varphi_0)]$$

or

$$\frac{d^2 Z}{d\lambda^2} - M^2 \tau_n^2 S^2 Z + M^2 \tau_n^2 S^2 \varphi_0 = 0. \quad (6.52)$$

Equation (6.52) usual second order differential equation with absolute term [166]. Total interval of this equation can be found in the form of the sum of the total solution of a homogeneous equation without an absolute term and partial

solution. In zero initial conditions we obtain the following solution:

$$Z = A_1 \exp(M_1 \tau_0 s) + A_2 \exp(-M_1 \tau_0 s) \quad (6.53)$$

For finding of image of function of speed, we differentiate equation (6.53) by  $s$  and substitute it into the equation (6.51a) then

$$W = \frac{A_1}{M_1} \exp(M_1 \tau_0 s) + \frac{A_2}{M_1} \exp(-M_1 \tau_0 s). \quad (6.54)$$

Equations (6.53) and (6.54) are equations of relative deviations of pressure and speed in images for combustion chamber.

Considered dynamic system is written, on one side, with partial differential equations (6.45) and (6.48), connecting speed and pressure in combustion chamber, and on the other side, with two equations for flow of fuel and oxidizer in ordinary or in partial derivatives.

For finding of characteristic equation of system it is necessary to write boundary conditions. As in the case with concentrated parameters we accept, that burning occurs at the head, where fuel, proceeding in combustion chamber burns during the time  $t = \tau$ . By means of linearization of equation of speed at the head of engine boundary condition can be obtained at the beginning of the chamber.

Second boundary condition for combustion chamber in critical section can be obtained in a similar manner, conducting linearization of equation of consumption in critical section.

So that the system of equations would appear closed, it is necessary to add equation of motion of components through pipe line to boundary conditions. Characteristic equation of similar system also provides conditions of stability.

Simplified characteristic equation was considered in work of Crocco [134]. This equation was obtained from analysis of the influence of small disturbances on the process in the combustion chamber, which is written in ordinary equations for one-dimensional steady-state flow. Boundary conditions can be found from the assumption concerning the fact that, the time lag is reciprocal to pressure in degree "n".

Using this assumption, it is easy to establish a law of change of pressure at the head of the engine. Conditions at the critical section in case of small disturbances are near to the steady-state conditions, i.e.,  $M = \bar{M}$  at  $x = \bar{L}$ .

Characteristic equation has the following form:

$$1 - B \exp(\alpha \theta) - \bar{M} \exp(-\alpha \tau) [1 - B \exp(\alpha \theta)], \quad (6.55)$$

where

$$\alpha = \lambda + i\omega; \quad B = \frac{1 - \frac{k-1}{2} \frac{\bar{M}}{M}}{1 - \frac{k-1}{2} \frac{\bar{M}}{M}};$$

$\theta$  — characteristic time of combustion chamber;

$\tau$  — time lag.

At a determined value of time of delay in chamber frequencies of oscillations are realized, near to frequencies of oscillations of column of gas in long pipes.

Stability of system is determined by value of ratio  $\tau/\theta$ . Changing  $\tau$  or  $\theta$ , it is possible to reach stable operating conditions of the engine.

The location of the front along the axis of the chamber has a large value for the appearance of high-frequency oscillations. In location of the front at injector nozzles of combustion there is the greatest tendency for instability [134], [138].

Analysis of system with burning in a narrow zone, as was shown, is accomplished mathematically simply, since propagation of disturbance is easily determined on the basis of acoustic solution of an ordinary wave equation.

In distributed burning the flow is no longer uniform and in this case the equations of motion will be distinguished from simple wave equations. Solution of such a problem can be carried out with the application of complicated mathematical methods.

Placement of a similar problem and its partial solution is listed in work [138].

#### Section 4. Analysis of Instability of a System with Distributed Parameters in Pipe Lines

We analyzed two forms of instability — low-frequency instability for a system

with concentrated parameters and high-frequency instability for a combustion chamber with distributed parameters.

Significant interest is presented by analysis of a system, having in its composition pipe lines for supplying the components with distributed parameters. Considerations of such a problem in general form does not present special complications. However construction of boundaries of stability in this case meets a number of difficulties.

We will conduct analysis of a one component system of liquid-fuel rocket engines, as this was carried out in work [137]. In conclusion of equation for combustion chamber are kept main assumptions, made in the first paragraph.

Let  $\bar{v}$  and  $\bar{p}$  be the speed and pressure in a pipe line in stationary conditions and let  $v'$  and  $p'$  be the corresponding small deviations from these conditions.

Equation of motion of liquid

$$\frac{\partial v'}{\partial t} = -\frac{1}{\rho} \frac{\partial p'}{\partial x} \quad (6.56)$$

Equation of inseparability

$$\frac{\partial^2 v'}{\partial x^2} = \frac{1}{a^2} \frac{\partial^2 v'}{\partial t^2} \quad (6.57)$$

where  $a$  is the speed of sound in the liquid.

From equations (6.56) and (6.57) it is easy to obtain a solution for  $v'$  and  $p'$ :

$$v' = \left[ K_1 \exp\left(\frac{\alpha x}{a}\right) + K_2 \exp\left(-\frac{\alpha x}{a}\right) \right] \exp(\alpha t) \quad (6.58)$$

and

$$p' = a\bar{p} \left[ K_1 \exp\left(\frac{\alpha x}{a}\right) - K_2 \exp\left(\frac{\alpha x}{a}\right) \right] \exp(\alpha t) \quad (6.59)$$

where  $K_1$  and  $K_2$  are the real constants.

$\alpha$  — complex value;

$x$  — distance from tank to head.

At constant pressure in tank at  $x = 0$   $p' = 0$ . At substitution of this condition into the equation (6.59) is clear that  $K_1 = K_2 = K$ . At  $x = \frac{l}{2}$  the boundary conditions

will be

$$v'_{x=0} = F_{\text{np}} k = W' \exp(\alpha t).$$

In the last equation  $W' \exp(\alpha t)$  presents a deviation of consumption from stationary condition and, consequently,  $W'$  — amplitude of this deviation.

According to this boundary condition

$$k = \frac{W'}{F_{\text{np}}} \frac{1}{\exp\left(\frac{\alpha l}{a}\right) + \exp\left(-\frac{\alpha l}{a}\right)}$$

and

$$v' = \frac{W'}{F_{\text{np}}} \frac{\exp\left(-\frac{\alpha x}{a}\right) + \exp\left(-\frac{\alpha x}{a}\right)}{\exp\left(\frac{\alpha l}{a}\right) + \exp\left(-\frac{\alpha l}{a}\right)} \exp(\alpha t).$$

According to Bernoulli equation

$$\frac{p_0 - p_x}{\rho} = \left(\frac{F_{\text{np}}}{F_{\Phi}}\right)^2 \left[\bar{v} + (v')_{x=0}\right]^2 \frac{1}{2} + \int_0^x \frac{d}{dt} (\bar{v} + v') dx;$$

Integrating the last member, we obtain

$$\begin{aligned} \frac{p_x}{\rho} &= \frac{p_0}{\rho} - \left(\frac{F_{\text{np}}}{F_{\Phi}}\right)^2 \frac{\bar{v}^2}{2} - \left(\frac{F_{\text{np}}}{F_{\Phi}}\right)^2 \frac{W' \exp(\alpha t)}{F_{\text{np}}} - \\ &- a \frac{W'}{F_{\text{np}}} \exp(\alpha t) \frac{\exp\left(\frac{\alpha l}{a}\right) - \exp\left(-\frac{\alpha l}{a}\right)}{\exp\left(\frac{\alpha l}{a}\right) + \exp\left(-\frac{\alpha l}{a}\right)}. \end{aligned}$$

Disregarding small deviations of the second order and differentiating equation (6.59), we obtain

$$\frac{1}{\rho} \frac{dp_x}{dt} = \left(\frac{F_{\text{np}}}{F_{\Phi}}\right)^2 \frac{v' W'}{F_{\text{np}}} \exp(\alpha t) - a \frac{W'}{F_{\text{np}}} \exp(\alpha t) \frac{\alpha l}{a}. \quad (6.60)$$

Equation of balance of mass in this case for chamber will be

$$W'_{(t-\tau)} = \frac{F_{\text{np}} F_{\text{np}} k}{C^*} + \frac{k' R T_0}{C^{*2}} \frac{dp_x}{dt}, \quad (6.61)$$

where

$$k' = \frac{1}{k} \left(\frac{k+1}{2}\right)^{\frac{k+1}{k-1}}.$$

$W'_{(t-\tau)}$  it is possible to write in the form of

$$W'_{(t-\tau)} = \bar{W} + W' \exp[\alpha(t-\tau)]. \quad (6.62)$$

where

$$\bar{W} = \frac{F_{\text{np}} k}{C^*} \left[ p_0 - \left(\frac{F_{\text{np}}}{F_{\Phi}}\right)^2 \frac{\bar{v}^2}{2} \right]. \quad (6.63)$$

After conversions of equation (6.54) we have

$$\exp(-\alpha t) = -\frac{2\Delta p}{\rho_k} - \frac{aF_{sp}}{c \cdot F_{TP}} \gamma_{sp} \frac{al}{a} - 2 \frac{\Delta p}{\rho_k} k'a - \frac{ck'v}{FC^2} \gamma_{sp} \frac{al}{a} \quad (6.64)$$

Equation (6.61) is frequent characteristic of the system.

We investigate the stability of the system, which is written by equation (6.64).

Let  $\alpha = -\lambda + i\omega$ , then at  $\lambda = 0$  equation (6.57) after division into real and imaginary parts takes on the form

$$\cos \omega t = -\frac{2\Delta p}{\rho_k} + \frac{ak'L \cdot F_{sp}}{F_{TP} c^2} \omega \gamma_{sp} \frac{\omega t}{a} \quad (6.65)$$

$$\sin \omega t = \frac{aF_{sp}}{F_{TP} c^2} \gamma_{sp} \frac{\omega t}{a} + 2 \frac{\Delta p}{\rho_k} \frac{L \cdot k' \omega}{c^2} \quad (6.66)$$

Solution of these two equations provides values  $\omega_{sp}$  and  $\tau_{sp}$ . Some of them are shown in Table 15 depending upon the length of pipe line.

Table 15

(a) $\omega$ rad/sec	(b) $\tau$ sec.	(a) $\omega$ rad/sec	(b) $\tau$ sec.
$l = 0,305 \text{ m}$		$l = 3,05 \text{ m}$	
552	0,00319	13	0,164
		97	0,040
$l = 3,05 \text{ m}$		122	0,016
122	0,0100	200	0,017
		231	0,0078
$l = 6,10 \text{ m}$		320	0,0105
62	0,031	340	0,0048
519	0,0050	432	0,0040
515	0,0031	447	0,0030
		544	0,00537
		556	0,0096

KEY: (a)  $\omega$  rad /sec; (b)  $\tau$  sec.

The investigations conducted show that depending upon the length of the pipe lines in the system of liquid-fuel rocket engines a whole spectrum of frequencies can appear.



## Section 5. Criterion of Shchelkin

Investigations of instability of zone of combustion in flat detonation wave, conducted for the purpose of determination of conditions of appearance by spin detonation, led Shchelkin to conclusion concerning possibility of use of results obtained for explanation of reasons of appearance of high-frequency oscillations in liquid-fuel rocket engines [158].

Let us consider the applicability of a method of analysis of instability of zone of ignition to burning in liquid-fuel rocket engines.

In Chapter VI it was indicated, that a thermodynamic and gas-dynamic picture of the process of combustion in liquid-fuel rocket engines is similar to combustion in detonation wave and is depicted by the lower arm of Hugoniot adiabatic line. On it lie thermodynamically real stationary methods of burning, determined by gas-dynamic states of flow in chamber of the engine.

A picture of the working process in the chamber of the engine can be shown schematically as it is depicted in Fig. 54.

In zone O-A occurs mixing and pre-flame processes. From plane A to  $\ast$  proceeds own burning. State of gas in plane A is determined by coordinates P-V on dynamic adiabatic line. As a result of high temperature and great density of products of pre-flame reactions combustion of fuel mixture occurs, which is finished in plane  $\ast$ . State of gas in this plane is determined by coordinates PV on Hugoniot diagram.

Distance between planes A and  $\ast$  is depth of zone of combustion and its magnitude is determined by time of chemical reaction.

Such a presentation concerning the process of combustion in the chamber permits us to affirm that in plane A is the forward boundary of front of detonation, but in plane  $\ast$  boundary of zone of combustion.

In case of appearance in plane  $\ast$  of disturbance with dimensions of zone of burning the loss of stability of front will be determined by the time of its stay in this zone and it will be disturbed at  $\tau \geq \tau_n$ .

We said it is possible to quantitatively formulate in the following manner. If as a result of disturbance of time of chemical reaction, or approximately the time of delay of ignition will grow to magnitude of order of actual delay or more, then arbitrary initial disturbance will lead to loss of stability of front.

Logical premises of such an order led Shchelkin to the creation of criterion of instability of zone of ignition in the form of

$$\frac{E}{RT} \left[ 1 - \left( \frac{p_A - \Delta p}{p_A} \right)^\gamma \right] \geq 1.$$

where T — temperature of heated mixture;

$\Delta p$  — loss of pressure in length of chamber due to combustion;

$\gamma$  — index of adiabatic line;

E — activation energy;

$p_A$  — pressure in plane A.

If width of disturbance of front of burning is known, then it is easy estimate the quantity of pulsations which, will be placed on area of section of chamber, and also zone of burning.

Calculation of criterion of instability for large quantity of mixtures shows that practically in all cases instability takes place.

At each disturbance in combustion chamber appears wave of pressure with fall of pressure  $\Delta p$ . However not any disturbance presents danger for engine.

In a case, if frequency of disturbance will occur in resonance with natural frequency of oscillations of gas (longitudinal, transverses), in chamber oscillations appear with falls in pressure dangerous for the engine. An estimation shows that pressure in wave of compression during resonance oscillations, if this will be possible according to conditions of durability of chamber, can attain order of magnitude of pressure in chamber.

One should note that results of analysis, obtained by Shchelkin are confirmed by experimental investigations of Berman and Chin, and also Elias and his collaborators [162]. In these works it was shown that high-frequency instability is characterized

by existence of waves of compression or shock waves, moving along combustion chamber from head of engine to nozzle and conversely.

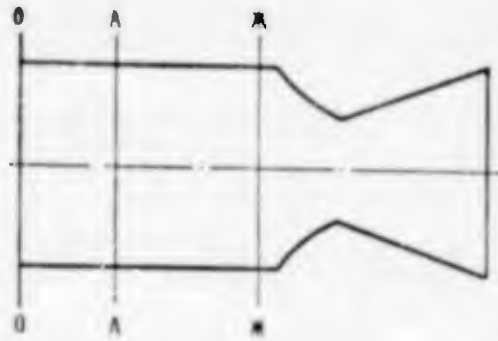


Fig. 54. Diagram of liquid-fuel rocket engine.

In the presence of high-frequency oscillations in combustion chamber periodically appear dark regions which indicates local fluctuations of temperature, and consequently, local heterogeneity of composition of mixture.

#### Section 6. Experimental Research of Stability of Process of Burning

Hydrodynamic theory of stability of burning in liquid-fuel rocket engine has a number of large gaps. First of them consists in the fact that in this theory the nature of the main parameter is not described —time of delay. Till now reliable measurements of time of delay were absent and it was not shown, in what connection is this magnitude with known positions of general theory of burning.

Analysis of a linearized model, which is conducted in many investigations, appeared to be one of the weakest places in the entire theory of stability.

Cause of this consists in the fact that analysis of original system is replaced by analysis, its linear model and in all works remains opened question concerning, in what measure obtained results on original model are spread.

As it is known, stability of linear model depends only on properties of system and does not depend on magnitude of initial deviation. In linear model possibilities are absent of appearance of undamped oscillations. In real systems it is possible

to observe, that after small initial deviations in system appear high-frequency oscillations. If however the magnitude of these deviations becomes larger than the determined value, then in system low-frequency oscillations are established.

Determination of sufficient conditions of unlimited stability can be carried out with the help of direct method of Lyapunov; in this case there should be conformity between theory and experiment.

Available literature on experimental data are incomplete, scattered in many sources and, consequently, cannot serve as material for thorough comparison with theory. Finally, last important shortcoming of theory is that the quantitative results, obtained in a number of works, it is impossible to generalize, since they were obtained without application of methods of theory of similarity.

The shortcomings shown are redoubled by difficulties, which appear during effectuation of experimental research in the field of stability. These difficulties consist in the fact that it is difficult to change only one parameter in system, not changing with this a number of other parameters. Another difficulty, peculiar to the process of burning atomized fuel, consists in the fact that the research, combined with study of this form of burning, is impossible to completely accurately reproduce and there always is significant scattering of results. This means that for obtaining reliable results are required large expenditures of time and means.

#### 1. Measurement of Time of Delay

Sensitivity of time of delay to conditions of injection of fuel and to processes, proceeding in combustion chamber, is according to hydrodynamic theory by main cause of instability of working process in liquid-fuel rocket engine. Therefore one of first problems of experimenters is confirmation of theory by means of direct measurement of time of delay, revealing of properties of this parameter and its dependence on the conditions in the chamber.

The difficulty in measuring time of delay lies not only in the necessity of

having accurate and reliable means for effectuation of experiment, but also in methods of approach to check of properties of time of delay. Method of "pulses", which are considered in detail in monography of Crocco and Sin Cheng [138], has a number of essential shortcomings.

If the pulse is applied to speed of injection, then it will affect the pressure in the chamber with delay. Assuming that the beginning of these two pulses is sharply defined, it is impossible to measure the interval of time between pulses and determine time lag. However, it is practically impossible to clearly determine the beginning of increase of pressure.

Since change of time of delay according to theory of stability depends also on pressure in combustion chamber, then leap of pressure is not finished in the moment, when the speed of burning falls again to normal, but its spread further due to relaxation of the process.

Thus, outside of the dependence on the form of the pulse (stepped or  $\Pi$ -shaped) it is difficult, and sometimes impossible to determine the time lag. The position is complicated in the absence of a sharply defined form of pulses. A more rational method of measurement of time of delay consists in the creation of undamped sinusoidal disturbances in the feeding system, which cause corresponding undamped fluctuations of pressure in the chamber.

Amplitude and phase displacement among these oscillations present themselves as a composite function of geometry of the chamber, nozzle, time of stay, time of delay etc. Connection of these magnitudes can be obtained with the help of theoretical expressions, introduced in works [159], [160].

A presentation concerning time of delay as concerning a definite physical conception allows to describe the process of burning in the engine chamber. This description becomes rigid, if we allow that in case of small sinusoidal disturbances time lag is equal for all particles of fuel. If speed of injection is correspondingly subjected to sinusoidal changes in frequency  $\omega$ , then their relative deviations can



be recorded in the form of

$$p_r = \frac{G_r - \dot{G}_r}{\dot{G}_r} \bar{p}_r \exp(i\omega t), \quad (6.67)$$

$$p_0 = \frac{G_0 - \dot{G}_0}{\dot{G}_0} \bar{p}_0 \exp[i(\omega t - \beta)], \quad (6.68)$$

where for the purpose of generality the phase delay of the disturbance is also taken for the oxidizer.

Pressure in the chamber  $p_k$  will fluctuate around its mean value  $\bar{p}_k$  with frequency  $\omega$ , but with phase delay  $\beta_r$ :

$$p_k = \frac{p_k - \bar{p}_k}{\bar{p}_k} = \bar{p}_k \exp[i(\omega t - \beta_r)]. \quad (6.69)$$

Equation of balance of mass for combustion chamber can be written:

$$\frac{dG_k}{dt} + \dot{G}_k = G_r, \quad (6.70)$$

where  $G_k$  — mass of gas inside combustion chamber;

$\dot{G}_k$  — mass speed of flow of gas through nozzle;

$G_r$  — mass speed of formation of products of combustion.

If we introduce relative deviations of pressure in combustion chamber and speeds of flow, then this equation takes on the form

$$\begin{aligned} \bar{p}_k \frac{d\varphi}{dt} + \bar{p}_k - n[\bar{p}_k - \bar{p}_k(t - \bar{\tau})] &= K[\bar{p}_0(t - \tau_0 - \theta) - \\ &- \bar{p}_r(t - \bar{\tau}_r - \theta)] + 2K[\bar{p}_0(t - \tau_0) - \bar{p}_r(t - \bar{\tau}_r)] + \\ &+ \left(\frac{1}{2} + H\right)\bar{p}_0(t - \bar{\tau}_0) + \left(\frac{1}{2} - H\right)\bar{p}_r(t - \bar{\tau}_r), \end{aligned} \quad (6.71)$$

where  $\tau_0$  — total time lag;

$\bar{\tau}$  — changing part of time of delay;

$\theta$  — time of stay of gas in chamber;

$n$  — indicator of interaction;

$H, K$  — parameters of composition of mixture.

A detailed account of conversion of equation (6.70) into the equation (6.64) is stated in works [134], [160].

If the relative deviations in pressure in combustion chamber and speeds of flow of components are assumed to be sinusoidal, as in the equations (6.67) and (6.68), equation (6.71) can be rewritten in form of expression (6.65), suitable for



analysis of experimental data:

$$R_r e^{i\theta_r} = \frac{e^{i\omega_r \bar{\tau}} [i\omega_r + 1 - n(1 - e^{-i\omega_r \bar{\tau}})]}{-K e^{i\omega_r \bar{\tau}} \left( \frac{p_0}{p_r} - 1 \right) + \left( \frac{1}{2} + H + 2K \right) \frac{p_0}{p_r} + \left( \frac{1}{2} - H - 2K \right)} \quad (6.72)$$

Equation (6.72) determines amplitude and phase angle  $\theta_r$  depending upon relationship between speed of flow of fuel and changes of pressure in chamber. A similar equation can be written for speed of flow of oxidizer. In the equation (6.72) four are unknowns  $\bar{\tau}_r$ ,  $\theta_r$ ,  $\bar{\tau}$  and  $n$ , all others are obtained from experiment. Two unknowns can be directly obtained from equation (6.72). As for the increase in frequency the value  $\omega_r$  in the numerator becomes predominant:

$$(\omega_r) \gg |1 - n(1 - e^{-i\omega_r \bar{\tau}})| \quad (6.73)$$

and unknowns  $n$  and  $\bar{\tau}$  can be excluded.

For  $\theta_r$  and  $\bar{\tau}_r$  the following equations are obtained:

$$\left( \frac{\omega_r}{R_r} \right)^2 = (A^2 + B^2)(1 + M^2) + (1 + 2AM) + \quad (6.74)$$

$$+ 2\{[A + M(A^2 + B^2)] \cos \omega_r \bar{\tau}_r + B \sin \omega_r \bar{\tau}_r\}, \quad (6.75)$$

$$\omega_r \bar{\tau}_r = \beta_r \arctan \left| \frac{A \cos \omega_r \bar{\tau}_r + B \sin \omega_r \bar{\tau}_r + AM + 1}{B \cos \omega_r \bar{\tau}_r + A \sin \omega_r \bar{\tau}_r + BM} \right|$$

where  $A$ ,  $B$ ,  $M$  — functions from composition of mixture;

$R_r$  — ratio of amplitude of fluctuation of mass speed of flow of fuel combustible to amplitude of fluctuation of pressure in chamber,

$\beta_r$  — introduced phase angle between flow of fuel and pressure in combustion chamber.

Unknowns  $n$  and  $\bar{\tau}$  can be calculated at low frequencies from equation (6.72) at constant values  $\theta_r$  and  $\bar{\tau}_r$ . To execute these calculations it is necessary from an experiment to determine in a stationary method: pressure in combustion chamber, pressure of feeding of components, speed of flows of oxidizer and fuel, temperature of gases in chamber. In a non-stationary method one should determine: amplitude fluctuations in pressure and feeding of components phase angles between pressure of injection and pressure in combustion chamber and frequency of sinusoidal disturbances. These general measurements are sufficient for calculation of four unknowns.

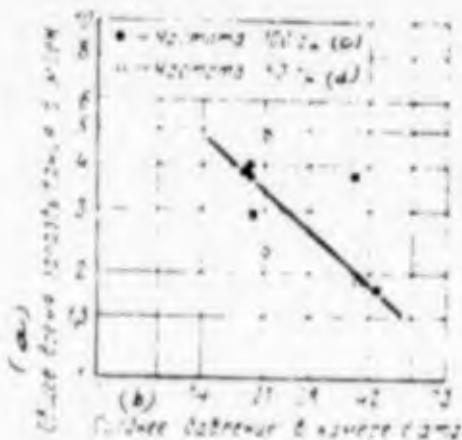


Fig. 55. Experimental dependence of total time of delay on pressure in combustion chamber [138].  
 KEY: (a) total time lag in millisecond; (b) average pressure in chamber in ata; (c) frequency 100 cps; (d) frequency 50 cps.

Measurement of time of delay at various pressures on single-propellant and bi-propellant engines show (Fig. 55) that the scattering of results is too great and difficult to determine the dependence of this magnitude on pressure in the established method. Which this scattering is a result of insufficient accuracy of measuring instruments or the result of the absence of such a connection between time lag and pressure, it is difficult to say.

Since time lag is not a physicochemical constant, then even reliable measurements of this magnitude solve only a small part of the problem, because immediately appears a question about how to use the results of measurements for other methods and other engines, i.e., how to generalize them.

## 2. Experimental Observations

In published researches [126]–[129] are described observations in the area of oscillations of low frequency and high-frequency instability.

The first form of oscillations appears in engines, that work at low injection pressures and low pressures in combustion chamber. With increase in pressure in combustion chamber stability of the system grows and simultaneously are developed

oscillations of high frequency. These observations are the result of a decrease of time of delay. By experiments it was established that frequency of oscillations in main lines corresponds to the frequency of oscillations of pressure in the combustion chamber. This circumstance indicates that the system of a liquid-fuel rocket engine is a dynamic system and at solution of problems of its stability it is necessary to consider the characteristics of its separate sections. The frequency of oscillations of the process increases with increase of characteristic length of engine.

Barrère and Moutet [153] from values of measured frequencies calculated the magnitude of the index of interaction and showed that it strongly depends on pressure in the chamber. Since these results were obtained from analysis of tests, which are made in the area of developed unstable oscillations, they cannot be considered fully reliable, and are only qualitative.

Principally important are investigations, conducted for the purpose of ascertaining the influence of the composition of a mixture on the stability of a system.

However the results obtained in work of Tischler and Bellman [128] do not correspond with the results Vasil'yev [161] and are evidently contradictory. The first show that the frequency of fluctuations is quite insensitive to fluctuations in composition of the mixture, and results of Vasil'yev [161] indicate that there exists two compositions of mixtures, with which appear unstable methods. Experimental investigations of Berman and co-authors, Tischler, Elias, and also ONERA in the field of high frequency show that this form of fluctuation appears at a definite length of the combustion chamber.

With an increase in the length of the combustion chamber stability becomes stronger, and frequency of oscillations falls. Measurements of distribution of pressure along length of chamber show that in case of high-frequency instability the pressures of wave, propagated both in a flow, and also against a flow are

important. The angle of conicity of the nozzle renders a strong influence on the stability of the system. A change in this angle leads to the fact that oscillations of high frequency can disappear and, conversely, appear.

In case of oscillations of high frequency there is an essential value just as at low frequency, fall in pressure on head, and impossible to accurately establish what is the cause, and what is the effect.

In conclusion we will show a comparison of experimental and calculated frequencies, which was carried out by Ross and Datner [129]. A combustion chamber, as these authors affirm, is possible to consider as a Helmholtz resonator. Such a resonator, as it is known, consists of a chamber with an aperture of small diameter and length. In the absence of a flow the rocket engine is like a resonator, and in this case it is possible by calculation to determine its resonance frequency.

Ross and Datner used a method developed by Elias and Gordon [162], in an analytic way determined resonance frequencies of a number of engines and compared them with experimentally obtained frequencies of unstable oscillations in working engines (see Table 16).

Table 16

(a) Диаметр камеры горения мм	(b) Отношение диаметра к площади критиче- ского сечения	(c) $L^*$ мм	(d) Частота	
			(e) эксперимен- тальная	(f) расчетная
108,7	1,5	1521	148	150
190,5	1,5	1270	308	300
378,5	3,6	1168	310	305

KEY: (a) Diameter of combustion chamber mm; (b) Ratio of diameter to area of critical section; (c)  $L^*$  mm; (d) Frequency; (e) Experimental; (f) Calculated.

## CHAPTER VII

### SIMULATION OF PROCESS OF BURNING

During designing of engines, it is necessary to solve the problem of how the process of burning occurring stably in a model is realized in a real engine.

Till now, similar problems were solved only by experimental means. We know that an experiment of such character is always connected with large risk and significant expenditures of time and means.

In spite of the fact that to avoid a similar experiment is impossible, a theory, which would determine necessary conditions of transition from model to engine significantly would ease the problem of creation of new engines.

Physicochemical conversion of atomized fuel in combustion chamber of liquid-fuel rocket engine is a totality of phenomena of chemical kinetics, hydrodynamics, and heat transfer; therefore, creation of rational design of engine is possible only during complex study of these phenomena.

Research in this region which would lead to qualitative results can be carried out in two different methods.

Essential peculiarity of first method of modeling of process of burning consists in that it can be described in the form of system of differential equations and the object of consideration will be separated by the region of changes of variable.

However, unfortunately, we must note that use of this method on an increased level of our kinetic knowledge is connected with insuperable difficulties. They

start from necessity of mathematical treatment of peculiarities of the process and terminate with the necessity of determining solutions of the system of differential equations. Such a solution is usually possible in the presence of simplifying prerequisites, significantly distorting the final results, which due to this lose practical meaning.

This method is applied to the theory burning. Here, a concrete case, characterized by definite geometric and physical conditions, is turned into an independent complicated problem. We cannot be concerned with any general results that would have been possible to use for any geometric form and any character of movement of gas or liquid in flow.

Second method consists in rejection of analytic solution. In it is used a way of experimental determination of protoplastic functions, i.e., way of application of theory of similarity and modeling. Theory of similarity indicates direction of experimental research and gives a method of mathematically processing of results.

Significant successes, attained by the theory of similarity in aerodynamics and heat transfer, i.e., in the areas, almost not treated by purely mathematical analysis, force us to think that these methods will give fruitful results during the study of the operating process of the liquid-fuel rocket engine.

This is explained by the appearance of a series of general researches devoted to the study of physicochemical processes with the help of the theory of similarity and, in particular, in the area modeling of process of burning.

During research of turbulent diffusion burning, Ivantsov [163], Petunin and Syrkin [164] applied elements of theory of similarity for simulation. They consider that at high temperatures of working process, speed of chemical transformation are so great that it does not limit the speed of process of burning, but reduces the phenomenon in the model and in the sample to autosimulation. In these conditions the main factor limiting the process of burning is turbulent mixing of fuel with oxidizer. Consequently, simulation may be realized during observance of three



conditions; a) identical temperatures in sample and model, b) the same fuel and c) identical hydrodynamic method.

Attempt of general analysis of similarity of chemical transformations were done in works of Danköhler [165]. Danköhler limited himself to consideration only of equation of motion viscous fluid and transfer equation of substance and heat. Criteria of similarity received by Danköhler, are insufficient for description of processes, where essential role is played by processes of transformation of original components.

Analysis of heterogenous chemical reaction proceeding on surface of solid phase by methods of theory of similarity, was conducted in work of Vulis [166], that showed that in most cases the criteria, determining flow of heterogenous reactions, are the criterion of Arrhenius (characteristic of kinetics of process), Péclet number (characteristic of diffusion) and the homochord number. Considered in this work, the examples sufficiently well illustrate expediency and perspectivity of processing of experimental data of methods of theory of similarity. Special value given by the author to the criterion of Arrhenius in the case when there is no confidence in the presence of real diffusion burning. Later, Vulis [167] expounded the rule modeling of a liquid-fuel rocket engine.

Solution of the problem connected with establishment of conditions of similarity, was carried out by Edgeworth and Jonston [168] for the hardly interesting kinetic region.

General conditions of similarity of physicochemical transformations for the first time were formulated by D'yakonov [169], [170]. Using extensive and fruitful researches of Academician M. V. Kirpichev and his school, the author showed large practical value of application of methods of theory of similarity during generalization of experimental data and obtaining of regularities for calculation of chemical reactors. Further development of these works is in the works of Norkin [171] and Usmanov [172].

Index of perspectivity of application of modeling of process of burning is also the use of widely known one-cylinder installations for determination of detonation stability of fuel (Vokesh, IG, NIT-9, etc.) and research on small liquid-fuel rocket engines [173]. The practitioner in the area of internal-combustion engine almost does not know of cases when there would be incongruity between appraisals received on model installation and real engine. Although the mentioned above modeling was carried out outside of the connection with theory of similarity, it is one of the largest technical proofs of expediency of application of theory of similarity during the study of processes of burning.

### Section 1. Main Aspects of Theory of Physicochemical Similarity

On the basis of study of phenomena, to which the present time was applied theory of similarity, are placed three main laws of physics: conservation law of matter, energy and pulse.

Mathematically, these laws are formulated by differential equations of material and thermal exchange and equations of motion of viscous fluid. System of these equations in vector form [174] are the following:

$$u_0 = -\operatorname{div}(\nu \operatorname{grad} c_1) + \operatorname{div}(D_1 \operatorname{grad} c_1), \quad (7.1)$$

$$Q_0 = -\operatorname{div}(\nu c_p \operatorname{grad} \theta) + \operatorname{div}(\lambda \operatorname{grad} \theta), \quad (7.2)$$

$$\rho \left[ \frac{\partial v}{\partial t} + (v \nabla) v \right] = \rho g - \operatorname{grad} p + \eta (\Delta v + \frac{1}{3} \operatorname{grad} \operatorname{div} v), \quad (7.3)$$

where  $u_0$  and  $Q_0$  — speed of material and thermal exchange;

$c_1$  — concentration of component.

Remaining magnitudes are in conventional designations.

Physical meaning of equation (7.1) consists in the fact that a definite element of volume is considered, in which the number of moles changes.

This change is determined by:

- 1) number of moles converted as a result of chemical reaction;
- 2) number of moles occurring in element of volume in unit of time;

3) number of moles diffusing in unit of time in the given element of volume.

Equation (7.2) describes quantity of heat delivered to element of volume from without by means of convection and thermal capacity, and also heat that will emanate in this volume as a result of reaction.

The left part of equation (7.3) expresses the relation between external forces acting on element of volume. In right part of this equation, the first member expresses force of external pressure and second expression in parentheses — frictional force.

Research of equations (7.1), (7.2) and (7.3) on invariance allows to receive criterion of similarity of studied process [175]—[179].

Detecting of conditions of similarity of model and sample is produced by means of comparison of two such cases, with which the flows for all magnitudes found in the equations (7.1), (7.2) and (7.3) are similar.

We shall give an example of how, from equation (7.3), one may receive the condition of hydrodynamic similarity. For that, we shall write equation (7.3) for axis X, whereby all entering magnitudes for the model will be supplied with marks as distinguished from magnitudes for sample:

$$\begin{aligned} & \nu' \left( v_x' \frac{\partial v_x'}{\partial x'} + v_y' \frac{\partial v_x'}{\partial y'} + v_z' \frac{\partial v_x'}{\partial z'} \right) = \rho' g_x' - \frac{\partial p'}{\partial x'} + \\ & + \nu' \left\{ \frac{1}{3} \frac{\partial}{\partial x'} \left( \frac{\partial v_x'}{\partial x'} + \frac{\partial v_y'}{\partial y'} + \frac{\partial v_z'}{\partial z'} \right) + \frac{\partial^2 v_x'}{\partial x'^2} + \frac{\partial^2 v_x'}{\partial y'^2} + \frac{\partial^2 v_x'}{\partial z'^2} \right\}. \end{aligned} \quad (7.4)$$

We shall designate

$$\frac{x'}{x} = A_l; \quad \frac{v'}{v} = A_v; \quad \frac{\rho'}{\rho} = A_p; \quad \frac{\nu'}{\nu} = A_\nu; \quad \frac{\eta'}{\eta} = A_\eta \text{ and } \frac{p'}{p} = A_p. \quad (7.5)$$

If we substitute values of variables with marks from equality (7.5) into the equation (7.4), we receive

$$\begin{aligned} & \frac{A_\nu A_l^2}{A_l} \left( v_x' \frac{\partial v_x'}{\partial x'} + \dots \right) = A_p A_\nu \rho' g_x' + \frac{A_p}{A_l} \frac{\partial p'}{\partial x'} + \\ & + \frac{A_\nu^2 A_\eta}{A_l^2} \left\{ \frac{1}{3} \frac{\partial}{\partial x'} \left( \frac{\partial v_x'}{\partial x'} + \dots \right) + \frac{\partial^2 v_x'}{\partial x'^2} + \dots \right\}. \end{aligned} \quad (7.6)$$

We consider similar such processes, for which values of  $A_l, A_v, A_\eta$ , etc. are such that multipliers standing before the brackets in the equation would have been

possible to reduce. For possibility of such reduction there should take place the following equality:

$$\frac{A_1 A_2}{A_1} = A_1 A_2 = \frac{A_1}{A_1} = \frac{A_1 A_2}{A_1} \quad (7.7)$$

Consequently, if the numerical values of  $A_1, A_2, A_1$  satisfy equality (7.7), then in the equation (7.6) the scale multipliers can be abbreviated; for model there remains an equation identical to equation of sample, and integrals of these equations also will be identical. From equality (7.7) we have

$$\frac{A_1 A_2}{A_1} = \frac{A_1 A_2}{A_1}$$

or

$$\frac{A_1 A_2 A_1}{A_1} = 1.$$

Having substituted in place of  $A_1, A_2$  etc., their values from equation (7.5), we receive

$$\frac{v l}{\nu} = \frac{v' l'}{\nu'} \quad \text{or} \quad \frac{v l}{\nu} = \frac{v' l'}{\nu'}$$

where  $\nu$  is kinematic viscosity. Invariant or dimensionless ratio  $v l / \nu$  is the known criterion of Reynolds  $Re$ . An analogous form can be received by other criteria of similarity.

Danköhler, being limited to consideration of system of equations (7.1), (7.2) and (7.3), received following criteria of similarity:

$$D_1 = \frac{a_1 u l}{c_1 \nu}, \quad D_{II} = \frac{u l^2}{c_1 D_1}, \quad D_{III} = \frac{Q u l}{c_1 \rho \nu}, \quad D_{IV} = \frac{Q u l^2}{\lambda \nu}, \quad Re = \frac{v l}{\nu} \quad (7.8)$$

where  $c_1$  — concentration in mole/cm<sup>3</sup>;

$a_1$  — stoichiometric relationship;

$u$  — chemical reaction rate in mole/cm<sup>3</sup>sec;

$Q$  — heat of reaction in cal/mole;

$D_1$  — diffusion coefficient in cm<sup>2</sup>/sec;

$v$  — speed of flow in cm/sec.

If we introduce time of conversion  $\tau$ , determined as the ratio of concentration to chemical reaction rate, then we receive

$$D_1 = \frac{a_1 l}{\nu \tau}, \quad D_{II} = \frac{a_1 l^2}{\nu D_1}, \quad D_{III} = \frac{Q l}{\nu c_1 \rho \tau} \quad (7.9)$$

The criteria of similarity of Dankeler have fully definite physical meaning:

$D_I$  — Ratio of the speed of formation of products of reaction to speed of removing these products by convection;

$D_{II}$  — Ratio of speed of formation of products of reaction to speed of removal of these products by diffusion;

$D_{III}$  — Ratio of speed of release of heat as a result of chemical reaction to speed of removal of heat by convection;

$D_{IV}$  — Ratio of speed of release of heat as a result of chemical reaction to speed of removal of heat by thermal capacity.

Consequently, upon disregarding radiation of heat, decisive for direction of stationary chemical processes are five dimensionless criteria: Reynolds number,  $Re$  and criterion  $D_I - D_{IV}$ . Equality of these criteria in two geometrically similar constructions of model and industrial apparatus is preliminary condition of similarity of fields of flow, concentration and temperature, due to which, in the model and industrial apparatus can be received the same yield of chemical reaction.

Analysis conducted by D'yakov [170], shows that the system of equations derived by Danköhler for establishment of physicochemical similarity is insufficient. Indeed, speed of transformation of original components is the result of the actual process and in the condition of uniqueness does not enter. Magnitude of this speed is determined both by the conditions of physicochemical transformation and the conditions of exchange. Therefore, determination of speed of the complex process requires joint consideration of equations of transformation and exchange, and isolated consideration of equations of exchange leads to description of the process, which is limited only to hydrodynamic peculiarities of system.

Exception of speed of reaction from the criteria of Danköhler leads to the usual Péclet number for material and thermal exchange and, consequently, criteria I—IV are useful only for analysis under the conditions of already existing similarity. Thus, the similarity of physicochemical transformations, considered by Danköhler,



is a particular case of the phenomenon. General conditions of similarity of physicochemical transformations were considered by D'yakonov also on the basis of the principle of conservation of energy, matter and pulse, but taking into account that the substances entering the reaction will be converted and change their nature.

Expression of principle of conservation of energy will be a proportionality between heat of transformation ( $Q_{II}$ ) and quantity of converting substance:

$$Q_{II} = -q \frac{dc_i}{dt} = \nu_i q u_i \quad (7.10)$$

where  $dc_i/dt$  is speed of conversion of component  $i$ ;

$q$  is thermal effect of reaction of transformation;

$\nu_i$  is stoichiometric number of component  $i$ .

Law of mass action in the consideration of physicochemical transformation expresses the conservation law of pulse, i.e., instantaneous value of rate of transformation is proportional to instantaneous quantity of converting substance:

$$u_i = -\frac{1}{\nu_i} \frac{dc_i}{dt} = \frac{1}{\nu_i} (K_1 c_A^{\nu_A} c_B^{\nu_B} - K_2 c_C^{\nu_C} c_D^{\nu_D}) \quad (7.11)$$

where  $c_A$  and  $c_B$  are instantaneous values of concentrations of original and final products;

$K_1$  and  $K_2$  — true constants of speed of direct and inverse processes, dependence on temperature of which is determined with the help of the equation of Arrhenius\*

$K_1 c_A^{\nu_A} c_B^{\nu_B}, \dots, K_2 c_C^{\nu_C} c_D^{\nu_D}$  are speeds of direct and inverse processes.

Equation (7.11) depicts total effect of reaction and its mechanism if reaction occurs without formation of intermediate products and equation of reaction corresponds to its mechanism.

Equation of conversion for reactions that go with the formation of intermediate products, can be written in the form of

$$-\frac{dc_i}{dt} = K_1^* \varphi_1(c_A, \dots, c_B) - K_2^* \varphi_2(c_A, \dots, c_B) \quad (7.12)$$

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\* $K_1$  and  $K_2$  refer to speed of transformation of component  $i$ .



where  $K_1^*$ ,  $K_2^*$  — effective constants of speed of direct and inverse processes;

$\varphi_1$  and  $\varphi_2$  — certain functions of concentration of substances participating in transformation depending on mechanism of transformation.

Stable physicochemical process is the dynamic equilibrium of process of transformation and process of exchange; therefore, it is possible to record

$$a_i u_n = u_0 - Q_n = Q_0. \quad (7.13)$$

Then

$$\frac{\partial \varepsilon_i}{\partial t} + K_1^* \varphi_1(c_A, \dots, c_B) - K_2^* \varphi_2(c_A, \dots, c_B, \dots) = -\operatorname{div}(\tau c_i) + \operatorname{div}(D_i \operatorname{grad} c_i)$$

and

$$\frac{\partial}{\partial t}(c_p \rho \theta) - q[K_1^* \varphi_1(c_A, \dots, c_B, \dots) - K_2^* \varphi_2(c_A, \dots, c_B, \dots)] = -\operatorname{div}(\tau c_p \rho \theta) + \operatorname{div}(\lambda \operatorname{grad} \theta). \quad (7.14)$$

Equation (7.14) is written without calculation of heat of radiation, constituting an insignificant quantity as compared to the total quantity of heat emanating in process of burning.

To equations (7.13) and (7.14) it is necessary to connect still an equation of motion

$$\rho \left[ \frac{\partial v}{\partial t} + (v \nabla) v \right] = -\operatorname{grad} p + \tau \left( \Delta v + \frac{1}{3} \operatorname{grad} \operatorname{div} v \right). \quad (7.15)$$

Research of system of differential equations (7.13), (7.14) and (7.15) on invariance allows to receive the following criteria of similarity for stationary process:

a) criterion of transformation\*

$$K_0 = \frac{K_2^* \varphi_2(c_A, \dots, c_B, \dots)}{K_1^* \varphi_1(c_A, \dots, c_B, \dots)}; \quad K_1 = K_1^* \varphi_1(c_A, \dots, c_B, \dots) t; \quad (7.16)$$

b) criterion of thermal and material exchange:  
criterion of thermal exchange

$$\operatorname{Pr} = \frac{\nu}{a}; \quad (7.17)$$

criterion of material exchange

$$\operatorname{Pr}' = \frac{\nu}{D_i}; \quad (7.18)$$

\* $K_0$  is usually called the criterion of contact.

c) criterion of proportionality of fields of temperatures and concentrations

$$\frac{q_{e_1}}{c_{\mu} \rho b}; \quad (7.19)$$

d) criterion of movement;  
Reynolds Number

$$Re = \frac{v l}{\nu}, \quad (7.20)$$

Froude Number (for flow during action of gravity)

$$Fr = \frac{K l}{v^2}, \quad (7.21)$$

Mach Number

$$M = \frac{v}{a}, \quad (7.22)$$

where  $a$  is the speed of sound,

Karman Number (for turbulent flow)

$$Ka = \frac{V \sqrt{w''^2}}{w''}, \quad (7.23)$$

where  $w''$  is pulsation speed.

In received system, criteria of thermal and material exchange and criteria of movement are universal and do not require special consideration.

Criterion of transformation  $Q_{II}$  is a measure of reversibility of process and characterizes the ratio of speeds of transformation and connection between concentrations of original and final products of reaction. It is necessary to indicate that burning of gas mixtures can be referred to maximum non-static processes with maximum shifted equilibrium towards the final products of transformation; therefore, criterion  $Q_{II}$  in such cases does not have to be considered.

Criterion  $K_0$  is a measure of the ratio of time of contact (or length of zone of transformation) to time of disintegration of original products of transformation.

The similarity of conditions of uniqueness will be attained at fulfillment of the following requirements formulated by D'yakonov:

- 1) identity of formulas of transformation (reaction);
- 2) geometric similarity;
- 3) similarity of laws of change of physical properties depending upon parameters of state and during transformation;

- 4) similarity of fields of variable and physical constants in initial moment;  
 5) similarity of conditions of material and power exchange on boundaries of system.

Depending upon character of solved problem, it is possible to present, on the basis of the theorem of Buckingham, a common integral of original equations in the form of a functional connection between criteria of similarity.

The most essential of the criteria is the criterion of quasistatic nature  $Q_{II}$  and first criterion of Damköhler. In accordance with this, it is expedient to have two forms for criterial equation of similarity:

$$Q_{II} = \Phi_1(K_0, Pr, Pr', \frac{vT_0}{c_l p^2}, Re, Ka, M). \quad (7.24)$$

$$D_1 = \Phi_1(K_0, Pr, Pr', \frac{vT_0}{c_l p^2}, Re, Ka, M). \quad (7.25)$$

Analysis of received conditions of similarity leads to the conclusion that full similarity is accessible only for simple cases of transformation. Together with that, from the complex process it is possible always to separate phenomena having a decisive role, and phenomena not essential for the given situation: in connection with this, different criteria of similarity will have various values. Criterion of similarity having essential value, are kept in criterial equation, but other criteria can be disregarded.

Modeling of process, carried out on the basis of such assumptions, is approximate. Theory of approximate modeling was created in Soviet Union by Academician Kirpichev and his school [177].

Analysis of processes of physicochemical transformations allows to establish three bordering cases and to formulate for them the condition of similarity.

1. If the process is thermodynamically balanced, then

$$Q_n = \frac{k_2^* \Phi(c_1, \dots, c_n, \dots)}{k_1^* \Phi(c_1, \dots, c_n, \dots)} = 1. \quad (7.26)$$

In this case the conditions of similarity are free from presentations concerning time and space.

2. If process of transformation proceeds in kinetic region, its kinetics will not depend on processes of transfer of substance and energy. Condition of similarity of such process does not contain requirements of geometric similarity, but criterial equation preserves only the criterion of chemical similarity:

$$Q_n = f(K_0, \dots). \quad (7.27)$$

3. If process of transformation proceeds in diffusion region, criterial equation does not contain determining criteria of chemical similarity and we receive

$$Q_n = f(Re, Pr, Pr', \dots). \quad (7.28)$$

## Section 2. Conditions of Similarity of Two-component Liquid Rocket Engine

Criterion of similarity, characterizing physicochemical transformation in model and in industrial apparatus, can be also used for approximate modeling of working process in liquid-fuel rocket engine.

As follows from equations (7.24) and (7.25), criteria of similarity for process proceeding in diffusion regions, are the following:  $Re$ ,  $Pr$ ,  $D_I$ ,  $D_{III}$ ,  $Ka$ ,  $M$  and  $Nu$  criteria characterizing the boundary conditions in combustion chamber.

For fuel vapor with definite physicochemical parameters, the  $Pr$  Number is constant in model and in industrial apparatus. Due to small speeds of flow, criteria  $Ka$  and  $M$  can be disregarded, and equality of initial temperatures predetermines that at constancy  $D_I$ ,  $D_{III}$  will be constant.

Using the expressed assumptions, let us consider a cylindrical combustion chamber with length  $l$  and diameter  $d$  [131], [180].

On the basis of equation of transformation, the ratio of second expenditures of components in engine  $M$  to model  $M$  will be

$$\frac{(v_0 A_0^2 N_0)_M}{(v_0 A_0^2 N_0)_m} = \frac{(v_r h_r^2 N_r)_M}{(v_r h_r^2 N_r)_m} = n. \quad (7.29)$$

where  $v_0$  and  $v_r$  -- momentum of oxidizer and fuel;

$h_0$  and  $h_r$  -- diameters of injector nozzles of oxidiser and fuel;

$N_o$  and  $N_r$  — number of injector nozzles of oxidizer and fuel;

$n$  — ratio of thrust of engine to thrust of model.

It is necessary to execute conditions of geometric similarity of chamber in order that

$$\frac{(d_r)_1}{(d_r)_M} = \frac{(d_o)_1}{(d_o)_M} = \frac{(l)_1}{(l)_M} = \frac{l_1}{l_M} = n \quad (7.30)$$

where  $d_r$  and  $d_o$  — distance between after burners of fuel and oxidizer, correspondingly;

$d_{r,o}$  — distance between after burners of fuel and oxidizer.

If the number of injector nozzles in the engine and in model are identical, then equation (7.29) will be copied as:

$$\frac{(v_o h)_1}{(v_o h)_M} = \frac{(v_r h)_1}{(v_r h)_M} = n \quad (7.31)$$

Condition of hydrodynamic similarity will be carried out, if the Re Number is identical. At constant coefficient of viscosity, the Re Number will be identical, if

$$(v_o v_o d)_1 = (v_o v_o d)_M \quad (7.32)$$

where index  $oo$  represents the fixed values of speed of oxidizer or fuel, and  $d$  — diameter of chamber. If the Re and Pr Numbers are constant, then the Nusselt Number is also constant.

In conclusion, chemical similarity will take place, if

$$(D)_1 = (D)_M \quad (7.33)$$

For combustion chambers with identical pressure  $p_o$  and  $p_n$  are constant. Combining equations (7.30) -- (7.33), we receive

$$\frac{(v_o)_1}{(v_o)_M} = \frac{(v_r)_1}{(v_r)_M} = \frac{1}{n} \quad (7.34)$$

$$\frac{(h^2)_1}{(h^2)_M} = \frac{(h^2)_1}{(h^2)_M} = n^2 \quad (7.35)$$

$$\frac{v_{o1}}{v_{oM}} = (n')^2 \quad (7.36)$$

In stationary conditions, speed of transformation of fuel per unit of volume is equal the quantity of proceeding fuel, divided by volume of combustion chamber:

$$u \sim \frac{p_o v_o h^2 N_o}{l d^2} = \frac{p_o v_r h^2 N_r}{l d^2} = \frac{p_r h^2 N_r}{l d^2} \quad (7.37)$$

at given stoichiometric relationship

$$\frac{\tau_{\Delta}}{\tau_M} = \frac{(L/\delta)_{\Delta}}{(L/\delta)_M} = \frac{(r \cdot h^2 N)_{\Delta}}{(r \cdot h^2 N)_{\Delta}} \quad (7.38)$$

After conversion of equation (7.38) with the help of equations (7.29)—(7.31), we discover

$$n' = n. \quad (7.39)$$

As a result, at  $(p_{\Delta}) = (p)_M$  and  $(\theta_o)_{\Delta} = (\theta_o)_M$  we receive

$$\frac{(v_o)_{\Delta}}{(v_o)_M} = \frac{(v_r)_{\Delta}}{(v_r)_M} = \frac{1}{n},$$

$$\frac{(d_{\Delta})_{\Delta}}{(d)_{\Delta}} = \frac{(d_r)_{\Delta}}{(d_r)_{\Delta}} = \frac{(d_o)_{\Delta}}{(d_o)_{\Delta}} = \frac{(l)_{\Delta}}{(l)_{\Delta}} = \frac{(d_{r.o})_{\Delta}}{(d_{r.o})_{\Delta}} = \frac{(h_r)_{\Delta}}{(h_r)_{\Delta}} = \frac{(h_o)_{\Delta}}{(h_o)_{\Delta}} = n,$$

$$\frac{\tau_{\Delta}}{\tau_M} = n^2.$$

Thus, speed of injection in model should be greater than in engine, by  $n$  times. All linear dimensions of model should be less than in engine, by  $n$  times. Time of transformation of fuel in model should be less than in engine by  $n^2$ . In connection this, it is necessary to recall that for diffusion region, mass speed of burning is a linear function of diameter of a drop.

Diameter of a drop will be

$$d_t^2 = d_0^2 - K't. \quad (7.40)$$

where  $d_t$  -- diameter of drop in relation to time;

$K'$  -- constant.

From equation (7.40) it follows where  $t$ -time of stay ( $\tau_s$ ) and  $d_t = 0$ :

$$\tau_s \approx d^2. \quad (7.41)$$

For well designed engines, where process of burning proceeds in diffusion region, it is possible to identify time of conversion with time of stay, and on the basis of equations (7.36), (7.39) and (7.41) write

$$\frac{d_{\Delta}}{d_M} = n' = n.$$

Condition of similarity can be formulated also for boundary of stability of stationary process of burning. If it is considered that one of the reasons for appearance of high-frequency oscillations in engine is interconnection between time



of conversion and time of propagation of wave along combustion chamber, then ratio  $\tau/\theta$  in engine should be the same as in model.

Time of conversion or time of turbulent burning

$$\tau = \frac{h_{r,0}^2}{D_t} \quad (7.42)$$

where  $h_{r,0}$  -- distance between after burners of fuel and oxidizer;

$D_t$  -- coefficient of turbulent diffusion.

Time of propagation of wave

$$\theta = \frac{d}{a} \quad (7.43)$$

where  $d$  -- diameter of combustion chamber:

$a$  -- speed of sound.

Thus, condition of similarity on boundary of stability will be kept, if

$$h_{r,0} \propto \sqrt{d} \quad (7.44)$$

Conditions of similarity for boundary of stability in the area of low-frequency oscillations can be formulated on the basis of conclusions that were received in this chapter.

Boundaries of stability in coordinates  $k$  and  $\tau$  are written

$$k\tau \sim \text{const} \quad (7.45)$$

If we introduce dimensionless time lag, using as scale  $\tau_0$ , then

$$k\tau/\tau_0 \sim \text{const} \quad (7.46)$$

Conditions of similarity will be kept, if expression (7.46) in the engine will be the same as in model.

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