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PHYSICS OF COMBUSTION
TEACHING MANUAL FOR STUDENTS

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The manual considers the fundamentals of the combustion theory and chemical kinetics of combustion reactions. The manual presents the theory of chain reactions, as well as the theory of thermal ignition (stationary, nonstationary). The normal combustion of laminar flames, the similarity of the distribution of temperature and concentrations in a flame, the formula for the normal velocity of flame propagation, the diffusion-thermal instability of a flame are described.

The manual is primarily intended for students of the Department of Thermophysics, but can also be useful for master course students, PhD and doctoral students.

Contents

Introduction

1.1 The concept of combustion

Usually any rapidly reacting chemical reaction accompanied by a release of heat and light is called combustion. From this point of view, substances can "burn" not only in oxygen. For example, many metals "burn" in chlorine, sodium and barium oxide "burn" in carbon dioxide, gunpowder burns without a gaseous medium, etc.

In the narrow sense of the word combustion is the reaction of combination of a substance with oxygen. To a greater or lesser extent, all substances are subject to combustion. Slow oxidation is also sometimes called slow combustion.

In this course we will consider only the processes associated with the presence of flame. More precisely, chemical reactions accompanied by luminescence and heat release will be called intensive combustion.

The process of combustion is one of a few natural phenomena whose discovery dates back to the earliest period of human history. The use of fire triggered harnessing of the forces of nature and played a special role in technical process in all further development of civilizations.

Fire became especially important when along with its use mainly for purely technological production purposes, it (combustion) became a means of production of mechanical energy (work). All this led to the high power-to-weight ratio, which characterizes the current state of technology.

In the Middle Ages, combustion processes especially attracted attention of chemists. At the beginning of the 18th century an attempt was made to combine all chemical facts on the basis of one hypothesis, to bring them into a system with the help of phlogiston theory. According to this theory, all substances able to burn or change under the action of fire contain a special "fire substance" –phlogiston. This theory, supported by all chemists of that time, dominated for a whole century.

In 1773, A. Lavoisier repeated experiments on calcination of metals and came to an explanation of combustion, as interaction of matter with oxygen, i.e. close to the modern views on the phenomenon of combustion.

Since that moment, our knowledge of combustion has progressed very much, and has served as the basis for creation of various combustion processes for a variety of purposes and mainly for energy generation.

It is well known that solid, liquid and gaseous fuels are burned in furnaces of power plants, and modern combustion devices have reached high capacities and a sufficiently high degree of perfection providing maximum combustion efficiency.

Internal combustion engines, which have developed rapidly in the last 100 years, use combustion of gases or vapor and liquid fuels and are used as the main engines in aviation and road transport. The efficiency of the reactive devices that emerged in the most recent years is even more dependent on the methods of burning fuel used in these engines. In fact, all the "military power" - artillery, rockets, missiles and other means of destruction, is based on the use of the phenomenon of combustion.

The combustion process is also widely used for various production purposes - for the organization of some chemical, metallurgical and other processes that require appropriate temperature conditions.

Knowledge of the properties and laws of combustion of various substances is very important, because in any field of technology the task of worldwide intensification of processes and ecological purity of production gets a high priority.

Any process of combustion or decomposition of substances is, primarily, a chemical process, as it is accompanied by the transformation of matter, a change in its quality. The study of the laws of compounds and transformations and conditions necessary for such transformations is the subject of chemistry. Chemical methods indicate in which direction and how deeply this or that reaction will pass. However, they do not provide information about the rates of transformation. This requires knowledge of some new properties of a combustible substance - its dynamic properties, manifested only in the process of transformation.

On closer examination of this problem, it turns out that in many cases of high practical significance, the combustion processes observed and used by us obey, first of all, purely physical laws. This situation is a consequence of the fact that the chemical transformation under certain conditions, for example, at a high temperature, can proceed at very high rates. The development of chemical transformation does not occur separately and independently of the actual physical situation and is accompanied by various physical phenomena that develop according to their own laws. As a result, the chemical process, with its development, often turns out to be regulated by such physical processes as heat transfer, diffusion and others. In other words, this means that *a chemical transformation with a very high potential in terms of its rapidity, is actually characterized by a rather limited speed and, in addition,* ***obeys the laws of some limiting physical phenomena, and does not follow purely kinetic laws.***

As an example we can take the case of burning of a coal particle at a sufficiently high temperature, when the reactivity of carbon is very high. In this case, the burning rate will be determined not by the speed with which carbon could react, but by the speed with which oxygen from the surrounding space flows to the coal particle. The supply of oxygen, for example, in the quiet air can only occur by diffusion. This purely physical process has relatively low velocities, and it is these speeds that will basically determine the combustion rate of the coal particle at high temperature.

In the case of combustion of gas mixtures, similar examples can also be found. When a premixed and, consequently, maximally reactive cold gas mixture is ignited by means of, for example, a spark near it, a small spot of the gas flame is created. In order for this flame to propagate farther along the entire volume of the gas mixture (cold), it is obviously necessary that from the region of the source a certain amount of heat be transferred to adjacent layers of the gas and heat them to the desired temperature. Under normal conditions, the transfer of heat is carried out by thermal conductivity, and in this case, naturally, the combustion rate of the mixture will be characterized by a value typical of the speed of the purely physical process of heat propagation.

There are many similar examples, and they clearly indicate a potentially large role of physical processes accompanying the phenomenon of combustion.

All the above information can be summarized as follows. The basis of the combustion process is the chemical transformation (reaction) associated with heat generation. *In the course of its development chemical transformation often entails the appearance of various physical processes*: heat transfer, transfer of reacting substances and other processes.

With the progressive development and acceleration of the reaction, these processes, at a certain stage, from independent and secondary processes *become the leading processes and determine the conditions of the reaction and intensity of chemical transformation* that caused their occurrence. As a result, combustion in accordance with its laws *from a qualitatively purely chemical process turns into a qualitatively purely physical process*, and the most part of this transition from one qualitative state to another occurs sharply, stepwise. This circumstance should always be kept in mind when analyzing the phenomena of combustion. Many examples of such processes will be given in further presentation.

All this means that *the combustion process must in general be regarded as a complex physical-chemical process whose speed is determined by the intensity of physical and chemical phenomena and the specific features of their interaction*.

This determines the tasks of the present course "Combustion physics" as a theory of physical processes and their role in combustion. This basically physical interpretation of the combustion process is sufficiently complete, concrete and practically justified.

1.2 Historical overview

Despite the fact that the phenomenon of burning was discovered by a man a long time ago, and there is a great practical experience of using it in various branches of technology, it is still hardly possible to speak of the physics of combustion as a fully developed and integral doctrine that unites in one theory the whole set of various experimental facts from combustion of gaseous, liquid and solid substances.

The main reason for this is the complexity of the nature of combustion processes, combining various physical and chemical phenomena in their interaction.

Statistical physics, heat transfer, hydrodynamics, and sometimes gas dynamics, as we will see below, have the closest relationship to the physics of combustion. All these circumstances greatly complicate investigation and description of the process.

The founders of the modern theory of normal combustion of gases are the French scientists Mallary and Le Chatelier and the Russian physicist, Professor V.A. Michelson. As early as in

1890 Mikhelson gave a deep analysis of this process in the pipes and the theory of flame on the Bunsen burner and theoretically substantiated the method of measuring the normal flame velocities with the help of a burner, which is well known now.

Not less important views were expressed by Michelson about the proliferation of the detonation mechanism. A few years later, Chapman presented the hydrodynamic theory of detonation. In his work, the only question that remained unresolved was justification of the regime that corresponds to what is observed in the experiment. The foundations for the solution of this question were contained in the work of Michelson, and only much later they served as the starting point for the solution of this problem by Ya. B. Zel'dovich.

In 1931, in Leningrad, Academician N.N. Semenov founded the Research Institute of Chemical Physics, which soon went to the system of the USSR Academy of Sciences and became the leading institute of the Soviet Union. Very important work was carried out by this institute during a relatively short period (10-15 years) in the study of ignition and burning of gases, which laid the foundations of the theory of the main combustion phenomena: the basis of the kinetics of chain reactions, the theory of thermal self-ignition, the theory of propagation of normal combustion, Semenov's theory of chain reactions received worldwide recognition and appreciation in the form of awarding the Nobel Prize to the author.

A great progress was made in the Soviet Union in the development of the physical-chemical basis for burning of solid fuels, mainly coal, as the basis of the general theory of heterogeneous combustion.

Progressively and quickly, especially in the period after the Second World War, research has been developing in the field of burning abroad. It was most noticeable in the United States, where numerous research institutes, educational institutes and universities with a large number of highly qualified physicists, chemists, mathematicians and technicians are working on the problem of combustion.

An important event for the development of combustion in all countries was the organization of systematic symposiums on combustion in the USA. Since 1948 these symposia have acquired an international character and attracted a large number of participants from different countries. Later similar symposiums (conferences) were held in the USSR. In 1986, the All-Union Symposium on Combustion and Explosion was held in Alma-Ata, which was a recognition of the scientific school on combustion created in Kazakhstan. The founder of this school is a world-known scientist Lev Abramovich Vulis. His disciples are famous Kazakhstani scientists: N.D. Kosov, V.P. Kashkarov, S.I. Isataev, K.E. Dzhaugashtin, S.A. Ershin, A.T. Lukyanov, L.Yu. Artyukh and many others who have numerous works on the physics of combustion, which have made a significant contribution to the development of this science. L.A. Vulis developed the theory of the thermal combustion regime, made a great contribution to the development of the theory of the stability of combustion, developed a method of the equivalent theory of heat conduction for calculation of diffusion flares.

1.3 Types of combustion

The vast area of combustion phenomena can be divided into two main groups:

1. Combustion of gaseous fuels – homogeneous combustion (characterized by a gas + gas system);
2. Combustion of solid and liquid fuels – heterogeneous combustion (systems: solid + gas or liquid + gas).

Recently, more and more attention is paid to burning of liquid-fuel + liquid-oxidizer systems, which can also be attributed to homogeneous systems.

Thus, ***homogeneous combustion*** *can be defined as burning of a system, all components of which are in the same aggregate state.*

First of all, let us consider the main characteristics of the process of gas burning, not only because of its great importance and deeper study of this process, but also because burning of solid and liquid fuels can always lead to burning in the gas phase.

In general, a gas system capable of burning consists of two kinds of substances – fuel and oxidizer, which chemically interact with each other in the process of combustion or explosion.

For two-component systems, in the predominant number of cases, one oxidizing agent is oxygen (the case of burning in the narrow sense of the word), and the second part can be any mixture of combustible gases. Both parts can, in addition, contain some non-combustible admixtures. For example, air contains 79% of nitrogen and only 21% of oxygen. In order for ignition or combustion to occur, it is necessary that before that, the active components of the gas mixture are mixed with each other.

From the very beginning it is useful to present two typical examples of gas systems. *Prior to ignition, the fuel and the oxidant can be carefully mixed with each other and thus create completely homogeneous initial conditions for the process.* We call such systems ***chemically homogeneous gas systems***.

In contrast, *ignition can be performed under the condition of a separated state of the combustible components at the beginning of the process.* In this case ignition and combustion occur in the process of simultaneous mixing and is based on more complex physical conditions. We call such systems ***chemically inhomogeneous***.

Both the first and second systems are equally encountered in practice of technical combustion of gases.

The chemical process, chemical transformation is the basis of combustion processes. Therefore, before studying the actual process of combustion of gases, it is necessary to get acquainted with the fundamentals of chemical kinetics.

Test questions:

1 What is the combustion process?
2 Give examples of combustion.
3 What processes accompany burning?
4 What is called homogeneous combustion?
5 Burning of which systems can be called homogeneous?
6 What systems are called homogeneous gas systems?
7 What are heterogeneous gas systems?

2 CHEMICAL KINETICS OF COMBUSTION REACTIONS

2.1 Stoichiometry coefficients

The generalized equation of the chemical reaction of combustion can be represented as follows:

$$\alpha A + \beta B = \gamma M + \delta N + Q. \qquad (1)$$

where: A is fuel, B is an oxidizer, M, N are reaction products; fuel and oxidizer are also called starting materials;

α, β, γ, δ are **molar stoichiometry coefficients**, they show the amount of substance of the given component involved in the reaction;

Q is **the thermal effect of the reaction (or calorific value of the fuel)**, it is the amount of energy released when 1 mole of fuel is burned, or 1 kg of fuel, or 1 m^3 of fuel. Accordingly, the units of measurement of the thermal effect can be the following: 1 J/mol, 1 J/kg, 1 J/m^3.

If $Q > 0$, the reaction is **exothermic** (proceeds with heat release), at $Q < 0$, the reaction is **endothermic** (proceeds with heat absorption). Obviously, all combustion reactions are exothermic.

For example, the combustion reactions of methane and hydrogen are written as follows:

$$CH_4 + 2O_2 = CO_2 + 2H_2O + Q, \qquad (2)$$

$$2H_2 + O_2 = 2H_2O + Q \qquad (3)$$

Let us calculate the mass of methane involved in the reaction, and the mass of oxygen necessary for its complete combustion (M is the molar mass):

$$m_{H_2} = \alpha M_{H_2} = 1 \cdot (14 + 1 \cdot 4) = 18 кг,$$

$$m_{O_2} = \beta M_{O_2} = 2 \cdot 16 \cdot 2 = 64 кг$$

Thus, to fully burn 18 kg of methane, it is necessary to use 64 kg of oxygen.

The amount of oxidant needed for combustion of 1 kg of fuel is determined by the **mass stoichiometry coefficient**:

$$\sigma_A = \frac{m_B}{m_A}. \tag{4}$$

Expression (4) is the definition of the mass stoichiometry coefficient for the oxidant. The mass coefficient of stoichiometry for oxygen in the reaction of methane combustion is 4.

We rewrite expression (4) as follows:

$$m_B = \sigma m_A \tag{5}$$

Formula (5) means the fulfillment of **the stoichiometry condition:** ***fuel and oxidizer are in a stoichiometric ratio, if they can react without residue.***

If more fuel is taken than is needed by the condition of stoichiometry (5), then it is said that the fuel is in abundance, otherwise it is in short supply.

Let us define the **molar concentration** as follows:

$$n = \frac{m}{MV} = \frac{\nu}{V}, \tag{6}$$

The molar concentration is **the amount of substance per unit volume.**

The amount of fuel per unit volume:

$$n_A = \frac{m_A}{M_A V} = \frac{\alpha}{V} \tag{7}$$

The amount of fuel per unit volume:

$$n_B = \frac{m_B}{M_B V} = \frac{\beta}{V} \tag{8}$$

Expressions (7) and (8) can be rewritten as follows:

$$\frac{n_A}{\alpha} = \frac{1}{V}, \quad \frac{n_B}{\beta} = \frac{1}{V}$$

It follows:

$$\frac{n_A}{\alpha} = \frac{n_B}{\beta} \tag{9}$$

This expression is a **stoichiometry condition for molar concentrations.**

2.2 Chemical equilibrium

To judge about this or that transformation, it is necessary to know the proportions in which the initial materials enter the compounds and the composition of the obtained products. The answer to this question is given by the fundamental classical laws of chemical statics: the law of conservation of mass (Lomonosov-Lavoisier) and the law of simple multiple relations (Dalton), as well as the theory of chemical equilibrium.

The theory of equilibrium is based on the law of acting masses – the fundamental law of chemical statics, first formulated in qualitative form by Guldberg and Vaage (1867) and later derived by Van't-Hoff (1885) on the basis of purely dynamic positions.

Practically all chemical reactions are reversible, i.e. it is more correct to write equation (1) as follows:

$$\alpha A + \beta B \leftrightarrow \gamma M + \delta N + Q.$$

Since the rate of reaction depends on the concentration of the starting materials in the mixture, at the initial instant of time the rate of the direct reaction is maximal. Then the concentrations of the starting materials decrease, hence the rate of direct reaction decreases, and the rate of reverse reaction, on the contrary, increases, as the concentration of reaction products increases, which for the reverse reaction are the starting materials. Thus, at some point in time there should be a situation when the rates of direct and reverse reaction equalize – this is the state of equilibrium.

The law of mass action *states that if a direct reaction between starting materials, for example A and B, and a direct reaction between direct reaction products, for example between M and N, is possible in a gas or other reaction system, then, if there is a sufficient time, there will always be an equilibrium between all reacting substances, characterized by the following relationship between the molar concentrations of these substances:*

$$\frac{n_A^\alpha n_B^\beta}{n_M^\gamma n_N^\delta} = K \quad , \tag{10}$$

where K is called the **equilibrium constant** and, according to Van't Hoff, depends on the temperature as follows:

$$\frac{d}{dT} \ln K = \frac{Q}{RT^2} \tag{11}$$

where *R* is the gas constant, and *T* is the absolute temperature.

The law of acting masses is not based on the assumption that physical parameters (temperature, pressure, etc.) do not change. In practice, the chemical equilibrium is never observed; in the real reacting systems, the temperature and pressure vary widely.

2.3 Reaction rate

If in a given volume the change in the concentration of substances occurs only as a result of a reaction and the diffusion process does not take place, then the rate of change in the concentration can be assumed to be the reaction rate.

*The rate of the **chemical combustion reaction** is equal to the amount of matter reacting per unit volume per unit time:*

$$w = \pm \frac{dn}{dt} \tag{12}$$

The rate of decrease in the amount of fuel is not equal to the rate of decrease in the amount of oxidizer, and therefore the reaction rates determined by the fuel and oxidizer are different:

$$w_A = -\frac{dn_A}{dt}, \quad w_B = -\frac{dn_B}{dt}$$

In the right-hand side of these equations there is a minus sign, as the concentrations n_A and n_B decrease. The rates of formation of reaction products are determined in a similar way:

$$w_M = \frac{dn_M}{dt}, \quad w_N = \frac{dn_N}{dt}$$

The right-hand side of these equalities have the plus sign, as the concentrations n_M and n_N increase.

In fact, there is only one rate of reaction, and it corresponds to a definite rate of heat release (or absorption); this quantity, in the final analysis, is essential for most questions of the theory of combustion.

In the existing classification of reactions, a class of so-called one-sided or "irreversible" reactions forms a special group. Unlike the reversible reactions mentioned above, in this case the reaction goes only one way and to the end, as there is no reverse reaction.

It must be noted that, strictly speaking, there are no irreversible reactions among gas reactions. At a sufficiently high temperature, the reverse reaction always becomes noticeable, therefore one can conclude that the gas reaction is irreversible only approximately, it means that we state that this reaction is an irreversible, one-sided reaction under the given conditions. This is the case with, for example, the widespread combustion reactions – combustion of carbon monoxide, hydrogen, and others, which, under normal combustion conditions in the air, can be considered as practically going to the end.

2.4 Reaction order

Irreversible reactions differ in their order, i.e. the total number of molecules joining the compound. In the notation of equation (6), the reaction order is equal to the sum:

$$\nu_1 + \nu_2 + \nu_3 + \ldots$$

According to Van't-Hoff's terminology, all "irreversible" reactions are divided into three groups: monomolecular, bimolecular and trimolecular reactions. The chemical equations corresponding to these three groups of reactions are recorded as follows:

monomolecular reactions, or first-order reactions:

$$A = M + N + \ldots$$

bimolecular reactions, or second-order reactions:

$$A + B = M + N + \ldots$$

trimolecular reactions, or third-order reactions:

$$A + B + C = M + N + \ldots$$

Higher-order reactions are assumed to be unrealistic in the molecular-kinetic theory, as the probability of a simultaneous collision of four molecules is negligible. In this case, the reaction proceeds, obviously, through simpler reactions and the usual presentation of the reaction by the chemical equation appears to be nothing more than a connection between the initial and final states of the system (stoichiometric ratio).

For the three types of reactions given above, the law of effective masses makes it possible to write the following kinetic equations. If molar concentrations of the substances formed at any time are designated as *m, n,* etc., then for the monomolecular reaction:

$$\frac{dm}{dt} = ka\left[\frac{\text{моль}}{\text{м}^3\text{с}}\right]$$

$$(13)$$

$$\frac{dn}{dt} = k'a\left[\frac{\text{моль}}{\text{м}^3\text{с}}\right]$$

where *K* and *K'*, etc. are called ***reaction rate constants***, *m*, *n* are the molar concentrations of substances *A* and *B*, respectively.

For the bimolecular reaction:

$$\frac{dm}{dt} = kab \qquad \left[\frac{моль}{м^3 с}\right]$$

For the trimolecular reaction:

$$\frac{dm}{dt} = kabc \qquad \left[\frac{моль}{м^3 с}\right]$$

It has already been noted above that the concentration corresponds to the number of molecules per unit volume. In practice mole concentrations - the number of moles per unit volume (unit of measurement - mol/m^3) or mass concentrations (with unit of measurement - kg/m^3) are used. It is also convenient to use the so-called relative (dimensionless) concentrations, which are the ratio of the number of molecules of a given substance to the total number of all molecules of the system per unit volume; in the case of gases they will also be equal to percentage concentrations. Obviously, depending on the choice of the method for determining the concentrations, the dimension of the constants will be different.

It must be remembered, that the absolute value of the velocity is ultimately determined by the molar concentrations that are functions of the pressure and temperature of the reacting system.

2.5 Dependence of the reaction rate on pressure

The value of the pressure has a significant effect on the rate of reaction, and the effect is different for reactions of different orders. Let us consider this question in more detail.

If the temperature remains unchanged, and we have a given composition of the initial gas mixture (given ratios of the components, that is, a given percentage composition), then according to the equation of state for each of the concentrations, we can write:

$$p_a = aRT,$$

$$p_b = bRT.$$

Here a, b, … are molar concentrations, p_a, p_b,... are partial pressures of the respective gases. If the total number of moles per unit volume is z, then in the same way for the total pressure in the mixture p, we get:

$$p = zRT.$$

It follows that

$$p_a = \frac{a}{z} p, \qquad p_b = \frac{b}{z} p.$$

$\frac{a}{z}, \frac{b}{z}, \ldots$ are relative volumetric concentrations. Denoting them by $A, B, \ldots$, we get

$$p_a = Ap, \qquad a = \frac{p_a}{RT} = \frac{p}{RT} A,$$

.

$$p_b = Bp, \qquad b = \frac{p_b}{RT} = \frac{p}{RT} B$$

Let us consider a monomolecular process:

$$\frac{dm}{dt} = ka = k\frac{p_a}{RT} = k\frac{p}{RT} A,$$

which means that the conversion rate in this case is directly proportional to the pressure:

$$\frac{dm}{dt} \sim p.$$

For a bimolecular reaction

$$\frac{dm}{dt} = kab = k\left(\frac{p}{RT}\right)^2 AB,$$

i.e. $\frac{dm}{dt} \sim p^2$ – the reaction rate is proportional to the square of the pressure.

Accordingly, for a trimolecular reaction, we obtain:

$$\frac{dm}{dt} = k\left(\frac{p}{RT}\right)^3 ABC \quad (12)$$

and $\frac{dm}{dt} \sim p^3$.

Hence it follows that for a reaction of the ν-th order

$$\frac{dm}{dt} \sim p^\nu.$$

It can be seen that the nature of the dependence of the rate of conversion on pressure can be used to judge about the order of the reaction. In view of this, by the value of the exponent of the pressure, we can also say whether the reaction is of the first, second or third order.

The experience shows that not always the order of reaction following from the chemical equation coincides with the observed order of reaction, in particular, with *the order* resulting from the dependence of the reaction rate on pressure; in particular, this is valid for multimolecular reactions.

2.6 Experimental determination of the reaction order

If two substances participate in the reaction, for example, carbon monoxide and oxygen, the form of the kinetic equation is:

$$w = \frac{dm}{dt} = ka^{v_1} b^{v_2} \, ,$$

where v_1 and v_2 are the unknown quantities that determine the order of the reaction for each of the components.

To find the values of v_1 and v_2 , two series of experiments should be carried out, each time keeping one of the concentrations unchanged and changing the other. As a result, the equation of the reaction in one case will have the form:

$$w_{\grave{a}} = k'a^{v1}$$

and in the other case

$$w_b = k''b^{v2}$$

where $k' = k\, b^{v2}, \; k'' = k'a^{v1}$

Taking the logarithm of these equations, we obtain:

$$lg\, w_a = v_1\, lga + lg\, k'$$

$$lg\, w_b = v_2\, lgb + lg\, k''$$

It is seen that in the system of $lg\, w$ and $lg\, a$ (or $lg\, b$) both dependences are represented as two straight lines, the slope of which determines the values of v_1 and v_2.

It is much easier to determine the total order in pressure from the value of w. According to the above, $w \sim p^{\nu}$, i.e. the reaction rate is proportional to the pressure in the power of ν if molecular concentrations are taken. Therefore, the graph of the dependence of $\lg w$ on $\lg p$ allows us, as before, to determine the values of ν by measuring the slope of the straight line with the $\lg p$ axis.

2.7 Reversible reactions

Reversible reactions refer to complex reactions. **Complex reactions** are reactions in which *several reactions independent of each other occur simultaneously, each of which obeys the law of acting masses*. For example, the rate of reversible reaction:

$$A + B \leftrightarrow M + N$$

Depends on two rates, so that

$$\frac{dm}{dt} = k_1 ab - k_2 mn .$$

In the equilibrium conditions $\frac{dm}{dt} = 0$ and

$$\frac{ab}{mn} = \frac{k_2}{k_1} .$$

According to (3) $\frac{ab}{mn} = K$, thus

$$K = \frac{k_2}{k_1} , \tag{15}$$

i.e. *the equilibrium constant K is equal to the ratio of the rate constants of the reverse and direct reactions*.

Typical gas reversible bimolecular reactions include the reaction of formation and decomposition of hydrogen iodide:

$$H_2 + J_2 \leftrightarrow HJ + HJ \tag{16}$$

Figure 1 shows this reaction as a function of time, obtained experimentally. The graph shows two curves: the upper one refers to the decay of hydrogen iodide, the lower one – to its formation. Both curves in the limit tend to the total limiting content *HJ* corresponding to the equilibrium content *HJ* for a given temperature

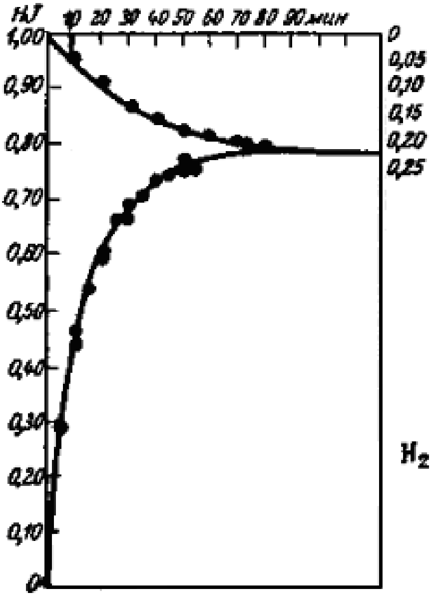

Figure 1 – Reaction $H_2 + J_2 \leftrightarrow HJ + HJ$
as a function of time; the upper curve is the decay of HJ,
lower curve - HJ formation

In the process of burning, typical reversible reactions are the reactions of dissociation of combustion products. For conventional fuels, these are vapors of water and carbon dioxide, the formation of which follows from the equations:

$$2H_2 + O_2 \leftrightarrow 2H_2O$$

$$2CO + O_2 \leftrightarrow 2CO_2$$

The equilibrium constants for these reactions are well-measured.

These reactions acquire practical value at very high temperature - about 2000^0C.

One of the characteristic features of the considered reactions (that is, reactions of the usual type, which follow the laws of classical kinetics) is the specific law of variation of the reaction rate with time in the case of isothermal flow of the process.

In reactions of any order, both reversible and irreversible, the reaction rate always gradually decreases in the course of reaction because of the decrease in the concentration of the starting materials. The highest reaction rate corresponds to the initial instant of time (Figure 2).

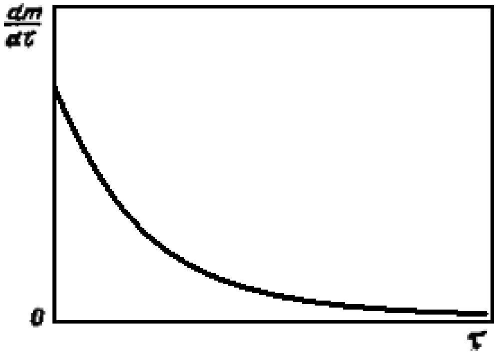

Figure 2 - Dependence of the reaction rate on time

This figure corresponds, as already mentioned, to the case of an isothermal flow of the reaction. In the case of non-isothermal conditions, the form of these curves will be different. The dependence of the reaction rate on temperature plays a very important role in this process.

It should be kept in mind that only a very small number of chemical reactions refer to reactions of the simplest type, i.e. mono- and bimolecular reactions. Chemical transformations, especially in the case of combustion reactions, occur through more complex transformations and in more diverse ways than indicated by the conventional chemical equation. The complexity and uniqueness of the observed combustion reactions is one of the reasons that triggered the development of a new type of kinetics – kinetics of chain and autocatalytic reactions, in which a very important role is played by kinetics of intermediate transformations.

Owing to the complex nature of the transformations, the overall behavior of the reaction in terms of dependence of the reaction rate on the concentrations of initial substances acting at a given moment never corresponds to the total chemical equation and, as a rule, does not give an integer order of the reaction. The latter can be fractional, just as there can be a fractional order for each of the components.

Moreover, the order defined as the sum of the values $v_1 + v_2 + v_3 + \ldots$ may not coincide with the order determined by the value of the exponent of pressure.

In view of all these circumstances, it is expedient to extend the concept of the order of the reaction (more precisely, the concept of the chemical process as a whole) by introducing a fractional-order reaction for each of the initial active components participating in the transformation.

This has a great practical meaning, as in any combustion process, in the end, the rate of combustion is determined by the total macroscopic or, otherwise, integral dynamic (kinetic) laws.

By analogy with the usual representation of the rate of reaction in the form of a product of a constant *K* at a given temperature and a function of the acting concentrations of the initial substances, we can generally write:

$$\frac{dm}{dt} = w = ka^{v_1} b^{v_2} c^{v_3} \ldots \tag{17}$$

where $v_1, v_2, v_3, \ldots$ in contrast to the previously mentioned, can be fractional numbers.

2.8 Dependence of the reaction rate on temperature

The most important achievement of chemical kinetics at the dawn of its appearance was the establishment of the laws of temperature variation of the rate constant of the reaction, the Arrhenius law. It follows from the experiment that the reaction rates increased very strongly with temperature.

On the basis of the experimental data Arrhenius found (1989) that for the constants of reaction rates in the general case, the equation is valid:

$$\frac{d}{dT}\ln k = \frac{E}{RT^2}, \tag{18}$$

where the quantity *E* is called ***the activation energy***, the physical meaning of which will be explained below.

Integrating the previous expression by the method of dividing the variables, we get:

$$\ln k = -\frac{E}{RT} + const$$

or

$$k = const\, e^{-\frac{E}{RT}}. \qquad (19)$$

The law in this form is known as *the Arrhenius law for the temperature dependence of the reaction rate constant.*

The equation (18) experimentally obtained by Arrhenius practically coincides in its form with the equation (4) obtained by Van't Hoff on the basis of theoretical calculations. The only difference is that the thermal effect of the reaction Q enters Eq. (4), and the activation energy E – Eq. (18). Using both these equations, and the relationship between the equilibrium constant and the rates of direct and reverse reactions (15), we can find how Q and E are related. From (4) with regard to (15) it follows that:

$$\begin{aligned} &\frac{d}{dT}\ln K = \frac{d}{dT}\ln\frac{k_2}{k_1} = \\ &= \frac{d}{dT}\ln k_2 - \frac{d}{dT}\ln k_1 = \frac{Q}{RT^2} \end{aligned} \qquad (20)$$

From (18) it also follows:

$$\frac{d}{dT}\ln k_2 = \frac{E_2}{RT^2}, \qquad \frac{d}{dT}\ln k_1 = \frac{E_1}{RT^2},$$

where E_1 is the activation energy of the direct reaction, and E_2 is the activation energy of the reverse reaction.

Hence,

$$\frac{d}{dT}\ln k_2 - \frac{d}{dT}\ln k_1 = \frac{E_2}{RT^2} - \frac{E_1}{RT^2} = \frac{E_2 - E_1}{RT^2}, (21)$$

As the left-hand sides of equations (20) and (21) are equal, their right-hand sides are also equal:

$$\frac{Q}{RT^2} = \frac{E_2 - E_1}{RT^2},$$

This implies the following equality:

$Q = E_2 – E_1,$

which gives the relationship between the thermal effect of the reaction and the activation energy, namely: the thermal effect of the reaction is equal to the difference in the activation energies of the reverse and direct reactions.

If $E_2 > E_1$, then $Q > 0$, therefore, the reaction is exothermic, i.e. goes with the release of heat; if, however, $E_2 < E_1$, then $Q < 0$, therefore, the reaction is *endothermic*, i.e. goes with the absorption of heat.

Theoretical considerations put forward by Arrhenius in support of this law are also based on the notion of equilibrium. Arrhenius suggests that a certain fraction of special reactive molecules is always in equilibrium in the gas system, and only these molecules, called "*active*" molecules, are able to react. The thermal effect of formation of active molecules is *E*, so this kind of "reaction" can be written as follows:

$A \Leftrightarrow I + E,$

where A denotes active molecules, I are inert molecules. By the law of acting masses, denoting the concentration of active molecules by a^* and inert via i, we obtain for the equilibrium constant K the following expression:

$$K = \frac{a^*}{i}.$$

Taking into account that for K the law is valid:

we get:

$$\frac{d}{dt}\ln K = \frac{E}{RT^2},$$

$$K = const e^{-\frac{E}{RT}}$$

The concentration always practically coincides with the total concentration of the molecules of the corresponding substance participating in the reaction (because of smallness of a^*, recall the Maxwell distribution). As for T $T \to \infty$ all molecules must be active, hence, $const = 1$. Then, denoting the total concentration of the molecules of matter by a, we obtain:

$$a^* = Ki \approx Ka = a\, e^{-\frac{E}{RT}} \qquad (22)$$

From here follows the sense of $e^{-\frac{E}{RT}}$ – it is a fraction of the molecules, their total number, able to react. The value of E, associated with the energy conditions of activation, is, therefore, called the ***activation energy***.

2.9 Relationship between the activation energy and the thermal effect of the reaction

These results concern a possible theoretical interpretation of the activation processes. Let us illustrate the relationship between the activation energy and the heat of reaction by the example of a certain system, the stoichiometric equation for the reversible reaction of which has a simple form:

$$A+BC \Leftrightarrow AB+C \pm Q \qquad (23)$$

This means that when the atom A collides with a molecule BC, it detaches one atom B from it and attaches it to itself. The value of Q is the thermal effect of this reaction. As a result of this reaction, we again get a diatomic molecule AB and a free atom C. We will consider this reaction in terms of energy.

The energy of a molecule is composed of its kinetic energy E and the binding energy of atoms in molecule D, which is negative. Thus, the total energy of any molecule is equal to E - D. We use the law of conservation of energy for our reaction:

before the reaction, the energy of the system is:

$$E_A + E_{BC} - Д_{BC}$$

after reaction: $E_{AB} - Д_{AB} + E_C$

By the law of energy conservation:

$$E_A + E_{BC} - Д_{BC} = E_{AB} - Д_{AB} + E_C$$

or

$$(E_C + E_{AB}) - (E_A + E_{BC}) = Д_{AB} - Д_{BC}$$

The left side of the equation is the difference between the kinetic energies of the reaction products and the initial molecules. It is positive if $Д_{AB} > Д_{BC}$, that is, with the formation of a more stable, more strongly-bound molecule, additional kinetic energy appears. As a result of this reaction, the mixture will be heated, as the growth of the kinetic energy of the moving particles is equivalent to an increase in temperature.

In the opposite case - with the formation of more "loose" molecules than the initial ones ($Д_{AB} < Д_{BC}$), the kinetic energy of the particles decreases, that is, the absorption of heat.

The difference between the kinetic energies of the final and initial products is called the ***thermal effect of the reaction*** Q ($Q < 0$ - endothermic reactions, $Q > 0$ - exothermic reactions). This is why Q is added to the right-hand side of the reaction equation (23).

Let's pay attention to the following circumstance. Equation (23) indicates that a reaction of this type can occur. But will it really proceed? Let us consider the reaction. For the *BC* molecule to collapse in a collision with an atom *A*, the initial system $A + BC$ must have a certain reserve of kinetic energy in order to break the bond between the *B* and *C* atoms.

However, one should not think that this kinetic energy should be greater than the binding energy D_{BC}, so that in the first stage of the reaction three free atoms *A, B,* and *C* can be formed. The reaction can proceed as follows: both stages of the reaction – collapse of the *BC* molecule and formation of *AB* molecule – occur simultaneously. The atom *B,* moving away from *C* (energy is absorbed), at the same time, approaches *A* (energy is released). With such a transfer of atom *B* from *C* to *A* ("from hand to hand"), the kinetic energy of the initial system required for the initiation of the reaction may be less than

D_{BC}. If the reaction is sequential (first, the *BC* molecule is split and then the *AB* molecule is formed), then the kinetic energy of the initial system $BC + A$ should be not less than D_{BC}.

The smallest excess energy that a colliding particle (a bimolecular reaction) or a decaying particle (a monomolecular reaction) should have, in order for a chemical transformation to occur, is called ***activation energy****.*

In accordance with modern views, the relationship between the energy of activation and the thermal effect of the reaction can also be illustrated with the help of the concept of an "energy barrier".

Let us imagine two energy levels I and II of a certain system, corresponding to the stoichiometric equation of the reversible reaction:

$$\mathrm{I} \Leftrightarrow \mathrm{II} + \mathrm{Q}$$

The transition from state I to state II from left to right is possible with the initial expenditure of energy E_1; reverse transition II → I is possible respectively at the initial energy expenditure E_2 (Figure 3). In this reaction, the energy is either released (I → II) or absorbed (II → I).

$$Q = E_2 - E_1.$$

The height of the potential barrier *E* is the minimum value of the kinetic energy that the system must possess in order for the chemical reaction to occur. The quantity *E* is called the activation energy, as only those particles will be chemically active, the energy of which is not less than the activation energy.

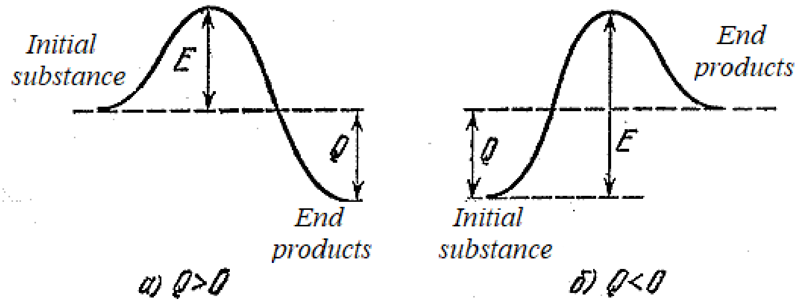

Figure 3 - Transition of the system from one state to another in exothermic (a) and endothermic (b) reactions.

Thus, *a chemical reaction occurs only between those atoms or molecules whose total kinetic energy is greater than or equal to the activation energy*. Therefore, it is very important to know the distributions of moving particles in the gas in terms of energies (velocities).

2.10 Molecular-kinetic basis for the Arrhenius law

It is known that in a gas heated to a certain temperature, not all molecules move with the same velocities. At each temperature, an equilibrium state is established in the gas, in which, despite continuous collisions and energy exchange between molecules, the fraction of molecules having energies in each energy interval remains unchanged. This fraction is determined by Maxwell's distribution law:

$$\frac{dN}{N} = \frac{4\upsilon^2}{\sqrt{\pi}\left(\frac{2kT}{\mu}\right)^{3/2}} e^{-\frac{\mu\upsilon^2}{2kT}} d\upsilon, \qquad (24)$$

which gives the ratio of the number of molecules *dN*, having velocities (by module) from *v* to *v* + *dv*, to the total number of N molecules. Here k is the Boltzmann constant ($k = \frac{R}{N_A}$, N_A is the Avogadro number).

This distribution is qualitatively shown in figure 4.

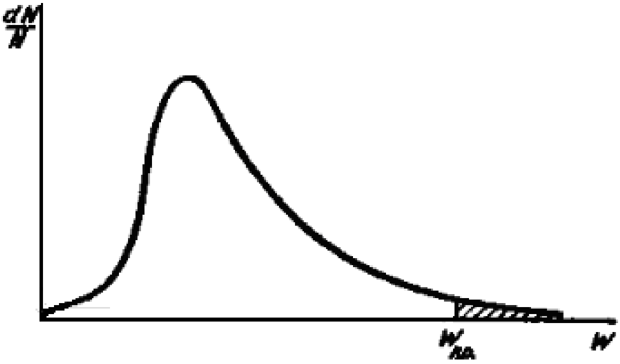

Figure 4 - Maxwell's distribution curve

The most probable speed is determined as follows:

$$\upsilon_{в} = \sqrt{\frac{2kT}{\mu}}$$

If we introduce a dimensionless velocity $u = \frac{\upsilon}{\upsilon_в}$, then (24) will have the following form:

$$\frac{dN}{N} = \frac{4\upsilon_в^2 u^2}{\sqrt{\pi}\upsilon_в^3} e^{-u^2} \upsilon_в du = \frac{4}{\sqrt{\pi}} e^{-u^2} u^2 du$$

We are only interested in "fast", reactive molecules whose velocity exceeds a certain critical value *u*'. What is the number of such molecules? Obviously, their number will be equal to the shaded area on the graph:

$$\frac{N_a}{N} = \int_{u'}^{\infty} \frac{dN}{N} = \frac{4}{\sqrt{\pi}} \int_{u'}^{\infty} e^{-u^2} u^2 du$$

It is difficult to compute this integral, but bearing in mind that *u'*>> 1, we can write its approximate value:

$$\left.\frac{N_a}{N}\right|_{u'>>1} \approx 1{,}128ue^{-u^2}$$

If we take the derivative of N_a/N with respect to *u*, we obtain:

$$-\frac{4}{\sqrt{\pi}} e^{-u^2} u^2 \approx 1{,}128e^{-u^2}\left(1-2u^2\right).$$

For large *u (u ≥ u')* the unit in the right-hand side can be neglected, and then this equality becomes an identity.

Hence, the number (fraction) of reactive molecules is determined by the expression:

$$\frac{N_a}{N} \approx 1{,}128ue^{-u^2} = 1{,}128\frac{\upsilon}{\sqrt{\frac{2kT}{\mu}}}e^{-\frac{\mu\upsilon^2}{2kT}}.$$

The quantity $\frac{\mu\upsilon^2}{2}$ is the kinetic energy of one molecule, $\frac{\mu N_a\upsilon^2}{2} \equiv E_\kappa$ is the kinetic energy of one mole of gas, then

$$\frac{N_a}{N} \approx 1{,}128\sqrt{\frac{E_\kappa}{RT}}e^{-\frac{E_\kappa}{2kT}}. \qquad (25)$$

The right-hand side of the expression is the fraction of molecules that has the kinetic energy higher than E_κ. If we assume that it is the kinetic energy of the translational motion of the molecules that activates the reaction energy, the resulting expression, which in its form is very similar to the empirical Arrhenius law, gives the physical content in a somewhat vague notion of active molecules and explains this law from pure physical positions.

Molecular-kinetic interpretation of the course of reactions is most directly applicable to bimolecular reactions. For each of the reacting gases *A* and *B*, one can write expressions for the number of molecules having an energy greater than some given values in the form:

$$a' = a \cdot 1{,}128 \sqrt{\frac{E_a}{RT}} e^{-\frac{E_a}{RT}}, \quad b' = b \cdot 1{,}128 \sqrt{\frac{E_b}{RT}} e^{-\frac{E_b}{RT}},$$

$\sqrt{\frac{E_a}{RT}}, \sqrt{\frac{E_b}{RT}}$ can be regarded as constants.

If the reaction rate is equal to the number of collisions of active molecules, i.e. $w = z' \quad \frac{1}{\text{м}^3 c}$ and as

$$z' = \pi r^2 \sqrt{\overline{\upsilon}_a^2 + \overline{\upsilon}_b^2}\, a'b'$$

where *r* is the sum of the radii of action of the colliding heterogeneous molecules, $\overline{\upsilon}_a$ and $\overline{\upsilon}_b$ are the average thermal velocities of these molecules, we obtain:

$$w = \pi r^2 \sqrt{\overline{\upsilon}_a^2 + \overline{\upsilon}_b^2} \cdot 1{,}128 \sqrt{\frac{E_a E_b}{R^2 T^2}}\, abe^{-\frac{E_a + E_b}{RT}}.$$

Let us denote:

$$1{,}128 \pi r^2 \sqrt{\overline{\upsilon}_a^2 + \overline{\upsilon}_b^2} \sqrt{\frac{E_a E_b}{R^2 T^2}} \equiv k_0,$$

Then we get:

$$w = k_0 abe^{-\frac{E}{RT}} \qquad (26)$$

Here k_0ab is the total number of collisions per unit time per unit volume, and E is the sum of kinetic energies of the two colliding molecules. In view of the latter circumstance, the activation energy of the bimolecular reaction is the sum of the kinetic energies of the two colliding molecules. For the reaction to occur, it is necessary that this amount be equal to a certain value characteristic of the given reaction. молекул.

Expression (26) shows that of the total number of colliding molecules of substances A and B, only a small fraction enters the reaction, and it is precisely those molecules whose total kinetic energy, in the collision, exceeds a certain critical quantity E. In such an interpretation, the quantity E has a purely thermal nature. The source of activation is an unordered thermal motion, which obeys the Maxwell law of distribution. The number of molecules that have kinetic energy above the value of E is the smaller, the greater this energy exceeds the average energy of the molecules of the system and the greater, the higher is the temperature of the system.

These results are not fully rigorous. The point is that Maxwell's law of distribution presupposes the presence of elastic collisions of molecules in the gas system. The presence of chemical processes in the system means, however, that the collisions are not elastic. Molecules, colliding, form pairs, and then either part again or enter into a close connection. Rotational and vibrational motions of molecules and atoms are also possible, as well as more complex energy changes within the molecules themselves, as a result of which the energy of the translational motion of molecules can become intramolecular or, conversely, intramolecular energy is released in the reaction. In all these cases, it also cannot be said that elastic collisions take place in the system. Nevertheless, the experience shows that the overwhelming number of reactions follow the Arrhenius law, even if these reactions are not simple, have a fractional order, etc. Why the reaction can have a fractional order, will be discussed later, but now we will pay attention to the experimental verification of the validity of the Arrhenius law.

The simplest way to verify the Arrhenius law for the temperature dependence of the rate constants of reaction, represented in the form:

$$k = k_0 e^{-\frac{E}{RT}} \quad (27)$$

and determine the values of k_0 and E is to represent the experimental data in the system *lnk* and *1/T*. Indeed, taking the logarithm of (27), we obtain:

$$\ln k = \ln k_0 - \frac{E}{R} \cdot \frac{1}{T}$$

This is the equation of a straight line in coordinates *lnk* and *1/T* with the angular coefficient $tg\alpha = E/R$ (Figure 5). Hence:

$E = R\, tg\alpha$ *J/mol*

The value of k_0 is determined from the value of the line segment cut off on the axis *lnk*.

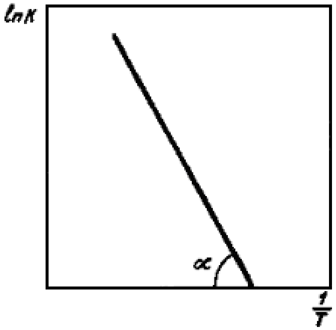

Figure 5 - Dependence of the reaction rate constant k on temperature

Test questions:

1 What are the mole coefficients of the reaction? What is the thermal effect of the reaction? What is the condition of stoichiometry?

2 What is the law of the acting masses?

3 How is the rate of the chemical reaction determined?

4 What is the order of the reaction?

5 How does the reaction rate depend on the pressure?

6 Record the Arrhenius law for the rate constant of the reaction.

7 How are the thermal effects of the reaction and the activation energy of the reaction related to each other?

2.11 Chain Reactions

2.11.1 Unbranched chain reactions

Experience shows that there are chemical reactions that do not need a noticeable pre-heating-up for their development. These reactions occur suddenly, are isothermal at low temperatures, and are characterized by rather high velocities. Such chemical reactions include, for example, cold flame phenomena during low-temperature oxidation of vapors of ether, phosphorus and various hydrocarbons.

Some chemical processes have the following special properties:

- The phenomenon of strong inhibitory or accelerating action of small amounts of impurities;
- the phenomenon of accelerating action on the reaction of its final products;
- the phenomenon of photochemical reactions, especially photochemical reactions of explosive type, such as, for example, the reaction of $H_2 + Cl_2$.

All these phenomena showed that in this case, activation cannot occur through the usual mechanism of thermal activation, which assumes that active molecules are represented by thermal motion, and their number is determined by Maxwell's law. There was obviously another reason and another effective source of activation that arose in the course of reaction itself and which did not require an obligatory preliminary significant heating of the reacting system.

The development of reaction kinetics from this point of view led to the creation of a new type of kinetics – kinetics of chain reactions and autocatalysis.

Molecules can be activated not only by the high energy particles in the "tail" of the Maxwellian distribution. The same can be done by supplying light energy to them. Each quantum of light absorbed by a molecule gives it its energy $h\nu$. If the quantum energy is sufficient (and this is determined by its frequency), the molecule is activated and reacts. In this case, we do not speak about a thermal reaction, but about a photochemical reaction. Thus, each quantum gives one transformation act, or, as it is said, in this case the quantum efficiency is unity.

However, this is not always the case. Due to different energy losses, the quantum efficiency can be less than unity.

In 1913, Bodenstein, studying the quantum efficiency of the reaction of formation of hydrogen chloride from gaseous chlorine and hydrogen, unexpectedly discovered a paradoxical fact. In this case, the quantum efficiency reached 105 and even more. In other words, the absorption of one quantum leads to hundreds of thousands of reactions, giving hundreds of thousands of molecules of the product – hydrogen chloride. From this discovery it follows that after the light-excited molecule of Cl_2 reacted with H_2, a long chain of transformations, already going without the participation of light, arose. Here, the first time the term "chain reaction" was used. But how can this happen?

The ordinary reaction $H_2 + Cl_2$, by analogy with the reaction $H_2 + J_2$, has to follow the bimolecular mechanism and the rates of these reactions should be close. Actually, the rate of the first reaction is many thousand times greater than the rate of the second. The required atomic chlorine is formed quite easily as a result of the dissociation of chlorine molecules upon absorption of a quantum of light, or with an increase in temperature and the collision of chlorine molecules with any sufficiently fast molecule M:

$$Cl_2 + h\nu \Leftrightarrow Cl + Cl \tag{28}$$

or

$$Cl_2 + M \Leftrightarrow Cl + Cl + M. \tag{29}$$

Atomic chlorine then readily reacts with a water molecule by reaction

$$Cl + H_2 = HCl + H. \qquad (30)$$

The activation energy of this process turns out to be small, of the order of 24000 J/mole, and therefore it proceeds much faster than the usual reaction

$$Cl_2 + H_2 \Leftrightarrow 2HCl,$$

for which $E \approx 16000$ *J/mole.*

As the concentration of chlorine atoms is usually low, and the activation energy of reaction (30) is 24000 *J/mole*, atomic chlorine would have to be consumed quickly. This is hampered, however, by the next link of the reaction, proceeding at an even faster rate, as a result of which the chlorine atom again appears:

$$H + Cl_2 = HCl + Cl \qquad (31)$$

and the reaction proceeds with a practically unchanged and, at the same time, a low Cl content. Such a mechanism makes it possible to proceed at a high rate. It should be noted that as a result of each elementary reaction a HCl molecule is formed and a free H or Cl atom is reconstructed. The process continues until the chain breaks off as a result of reaction $Cl + Cl = Cl_2$ or $H+Cl = HCl$, or the interaction with the wall.

Intermediate reaction products - chlorine and hydrogen atoms, which accelerate the formation of the final HCl product and play the role of catalysts, are called ***active centers****.*

From the consideration of this chain process it is clear that, when it proceeds, the number of active centers remains unchanged. *Chemical reactions proceeding along the chain* *mechanism, during which the concentration of active sites remains constant, are called* ***unbranched*** *chain reactions*.

As active centers are formed during the reaction and play a role of catalytic agents, such chemical reactions are called **autocatalytic**.

2.11.2 Branched Chain Reactions

The other type of chain reaction, in which each cycle or each elementary reaction will supply more than one active particle, is also possible. In this case, the number of active centers will continuously increase over time and spontaneously grow, and with it the reaction rate will also increase. The process becomes self-accelerating, like an avalanche process. In this case, the process is nonstationary and can spontaneously move from almost imperceptible changes to a violent and powerful response.

It is this kind of phenomena that is characteristic of explosive processes. *Chain reactions associated with a progressive increase in the number of active reaction centers are called branched chain reactions.*

An example of this kind of reaction can be a widely known reaction of a hydrogen connection with oxygen:

$$2H_2+O_2=2H_2O.$$

The actual course of the process does not obey this equation, which corresponds to a tri-molecular reaction. The most likely scheme of the reaction is the following.

The initial process

$$H_2+M=H+H+M \quad (32)$$

is a process of ordinary thermal dissociation. The follows a series of individual elementary acts:

$$\left.\begin{array}{l} H+O_2=OH + O, \\ O+H_2=H + OH, \\ OH+H_2=H + H_2O \end{array}\right\}\quad \text{1-st cycle} \qquad \begin{array}{r} (33) \\ (34) \\ (35) \end{array}$$

$$\left.\begin{array}{l} H+O_2=OH+O, \\ O+H_2=H+OH, \\ OH+H_2=H+H_2O, \end{array}\right\}\quad \text{2-nd cycle}$$

and so on.

Reaction (35) is a consequence of (33) and (34) and actually occurs twice, corresponding to two formed *OH* radicals. After the reaction (35), the sequence of the same reactions (33), (34) and the doubled reaction (35) again begin, etc. In this process, the number of hydrogen atoms progressively increases, and the entire reaction cycle is accelerated.

To determine the content of atmospheric hydrogen, at which the reaction becomes noticeable, some time is needed. This time was called the ***induction period of the reaction****.*

Thus, unlike all the reactions considered so far both ordinary and chain (unbranched) reactions with ordinary chains, in this case the development of the reaction is such that first the reaction is invisible, then it spontaneously increases to very large but finite values of speeds and only then begins to decline as a result of expenditure of reacting substances.

In Figure 6, which gives the dependence of the reaction rate on time, τ is the induction time. An unlimited increase in the concentration of hydrogen atoms is hampered by the process of their death, which is caused by a number of reasons, but mainly by the reaction:

$H+O_2+M=HO_2+M$

and the reverse reaction (32), the recombination of hydrogen atoms into molecules.

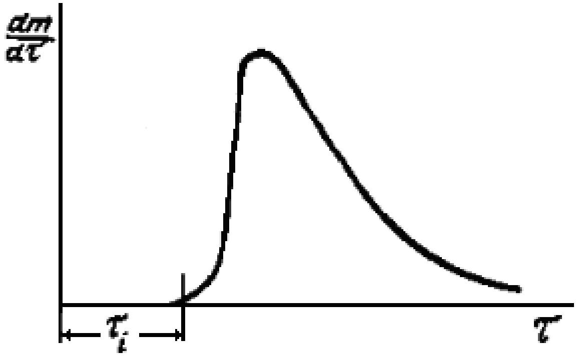

Figure 6 - Change in reaction rate with time;
τ is the induction period.

When the amount of atomic hydrogen becomes significant, its further increase ceases, and the reaction must become a stationary reaction. At the same time, the number of other active intermediate products, *O* and *OH*, does not increase any more.

In fact, the reaction rate does not remain constant after a rapid increase, as the quantity of reacting substances continuously decreases and accordingly the content of active centers decreases in the system. This decrease occurs, however, more slowly than accumulation of centers at the beginning of the process, and their number is in accordance with the amount of combustible substances in the reacting system; in this case, such are hydrogen and oxygen.

All the arguments, that have been given so far on the course of the reaction in time, refer to the so-called isothermal reactions. In the case when the temperature rises in the course of the reaction, the picture of the process is highly complicated and, as it will be shown below, self-acceleration of the reaction and appearance of an explosive effect will also occur in the case of a usual Van't Hoff kinetics.

Let us note in conclusion that the merit in the creation and wide development of the theory of chain reactions belongs to N.N. Semenov and a group of his disciples. As early as 1927 Semenov first directly applied the idea of chain transformations to the phenomena of inflammation, most important phenomena in practice and theory of combustion.

2.11.3 Total kinetics of complex reactions

In the practice of combustion and calculation of the process, it is necessary to know the overall or final kinetic equation of the chemical process, that is, it is necessary to know the effective rate constant of the reaction (its temperature dependence) and the order of the process for each of the initial substances involved in the reaction.

Examples of calculation of chain reactions show that the total reaction rate, at least for the unbranched chain, is always presented by an ordinary kinetic equation.

Finally, only these effective total kinetic laws should be taken into account in the complex interaction processes of physical and chemical factors forming the basis of combustion physics, as only the total rate determines the yield of reaction products and accompanying heat release.

Thus, in the future we will often use the approximate empirical equation determining the rate of the chemical reaction in the form:

$$W= W_T(T)W_C(C)= -dc/dt, \tag{36}$$

where

$$W_T = k(T)=k_0\, e^{-E/RT.} \qquad (37)$$

k_0 in the first approximation is considered independent of temperature.

We have already discussed the meaning of the quantities k_0 and E (k_0 corresponds to the number of collisions, E is the minimum value of the energy of the molecule, which provides the collision efficiency – the reaction). However, in what follows we will consider them as reduced empirical constants, which approximately reflect the total dependence of the reaction rate on temperature.

Let us consider in more detail the quantitative aspect of this dependence, which is extremely important for further presentation. For ordinary values of activation energy (approximately about $8 \times 8{\cdot}10^4 \div 16{\cdot}10^4$ kJ/mol) for simple chemical reactions, a dramatic impact of temperature on the reaction rate can be seen from Table 1.

Table 1

Values of the activation energy for different temperatures

Temperature *T, K*	Value $k/k_0=e^{-E/RT}$			
	$E=8{\cdot}10^4$ *kJ/mol*		$E=16{\cdot}10^4$ *kJ/mol*	
500	$2{\cdot}10^{-9}$	1	$4{\cdot}10^{-18}$	1
1000	$4{\cdot}10^{-5}$	$2{\cdot}10^{4}$	$2{\cdot}10^{-9}$	$5{\cdot}10^{8}$
2000	$6{\cdot}10^{-3}$	$3{\cdot}10^{6}$	$4{\cdot}10^{-5}$	$1{\cdot}10^{13}$

As can be seen from this table, a double increase in temperature at $E = E=8{\cdot}10^4$ kJ/mol and transition from 500 K to 1000

K, leads to a 20,000 increase in the function $e^{-\frac{E}{RT}}$ and a 500 million increase at E = 16 · 10^4 kJ/mol and the same temperature values.

A similar increase in temperature (from 1000 K to 2000 K) causes an increase in the reaction rate constant *k(T)* by 150 times at the first and by 20 thousand times at the second value of the activation energy. The above example shows how strong is the influence of temperature on the rate of chemical reaction. It also shows the possibility of neglecting in quantitative calculations weaker (power-law) temperature dependences compared with exponential (if they enter as a multiplier at $e^{-\frac{E}{RT}}$).

It can also be seen from the table that with an increase in the absolute temperature, the influence of the factor $e^{-\frac{E}{RT}}$ on the reaction rate weakens.

Let us also briefly consider the dependence of the rate of reaction on concentration. For the simplest reactions, the function W_C (c) in equation (36), according to formal kinetics, can be represented as a power-law dependence on the concentration of initial substances.

We have previously noted that for the ν-th-order reaction, ($\nu=\nu_1+\nu_2+\nu_3+...$ are stoichiometric coefficients). $W_C(c) = c_A^{\nu_1} c_B^{\nu_2} c_C^{\nu_3} \dots$. But if the substances in the mixture are in the stoichiometric ratio, then $c_A \sim c_B \sim c_C \dots$ and, consequently, $W_C\ (c) \approx c^\nu$, where ν is the reduced order of the reaction.

It should be noted that the equation

$$W_C\ (c) \approx c^\nu, \tag{38}$$

which we will use later in its simplest form ($\nu = 1$), does not describe the actual mechanism of the chemical reaction. It reflects, however, as can be seen from the formula:

$$W = k_0 c e^{-\frac{E}{RT}} \tag{39}$$

general and very important (in further presentation) property of simple chemical reactions, namely: the decrease in the reaction rate at a constant temperature as the initial product burns out and, consequently, the collision probability decreases between the reacting molecules. It also follows from Eq. (38) that when the combustion of the initial mixture is taken into account, the rate of the reaction in the final stage inevitably decreases, and in the limit, with complete disappearance of the initial products. This property is essential for studying the thermal combustion regime.

Thus, the expression for the reaction rate, reflecting the properties of the combustion process, which are the main properties for studying the thermal regime, we write, taking into account expressions (36) - (38) in the form:

$$W = k_0 c^{\nu} e^{-\frac{E}{RT}} \tag{40}$$

and for the simplest and, therefore, the most convenient case for qualitative calculations, $\nu = 1$, in the form (39).

Under normal ignition conditions, when the initial temperature is low and the concentrations of the reacting substances have the maximum values, the adiabatic reaction is always explosive. From this point of view, the adiabatic reaction, no matter how slow it is at first, will become noticeable from a certain point in time.

The interesting properties of adiabatic reactions considered here are of direct relevance to the case of burning, since for this process the main condition is the large exothermicity of the transformations and powerful self-heating of the reacting system. In reality, however, it is always necessary to take into account heat dissipation.

Test questions:

1 What reactions are called chain reactions?

2 What are branched chain reactions? What are their differences from unbranched chain reactions?

3 What are autocatalytic chain reactions?

4 What is called the induction period of the reaction?

5 How does the reaction rate change with time?

3 THE THEORY OF THERMAL EXPLOSION

3.1 Two types of ignition.

In order to start burning of the gas mixture, it is necessary to create certain initial conditions in the system – to ignite the mixture. Experience indicates the possibility of two methods that can be used to ignite gas mixtures. In practice, both methods are widely used.

In the first method all the ignitable mixture is brought to a temperature above which it independently ignites without external influence.

In the second method the cold mixture is ignited at only one point in space by means of a temperature source (usually a spark, a heated body, an extraneous flame, etc.) and further ignition of the entire volume of gas occurs without external intervention spontaneously, but with a certain spatial velocity of propagation of the burning rate.

According to these two methods of ignition they are called ***self-ignition*** and ***forced ignition, forced inflaming or simply ignition***.

Characteristics of both processes turn out to be very different, but they are based on the action of one common factor – the thermal factor.

As in practice there is a warm-up of the system and the associated thermal excitation of reactions, it is natural to consider the phenomenon of ignition from the positions of the thermal mechanism of the process. This is especially useful because it will make it possible to form a clear physical picture of the phenomenon and to understand the essence of the basic characteristics of ignition, which are convenient and important for combustion practice.

3.2 N.N. Semenov's theory of thermal explosion

3.2.1 Heat emission and heat removal curves

We know that the rate of chemical transformations depends on the composition of the mixture (the amount of initial substances) and the temperature. In real conditions and, especially in the case of combustion phenomena, the thermal conditions in the reacting medium are, firstly, determined by the process itself and, secondly, can never be homogeneous. In reality, ignition or combustion always occurs in a limited volume. The released heat is somehow lost in the environment, which leads to the occurrence of larger or smaller temperature differences within the reacting system. This difference in temperature entails a difference in the reaction rates at different points in space and appearance of an inhomogeneity in the composition of the mixture along with temperature inhomogeneity.

The area, more distant from the walls of the vessel, is characterized by a larger number of reaction products and a higher temperature. The layers adjacent to the walls will be colder, but there, accordingly, more initial products of the reaction will be present. As a consequence, in this system the transport phenomena of both heat and matter inevitably arise, and in order to analyze the process in this case it is necessary to solve a system of two differential equations: the heat transfer equations and the diffusion equations, which even in the simplest case of the reaction <u>in a stationary medium</u> have the following form:

$$-\frac{\partial c}{\partial t} = div(DgradT) - k_0 c^{\nu} e^{-\frac{E}{RT}} \qquad (41)$$

$$\rho c_p \frac{\partial T}{\partial t} = div(\lambda gradT) + qk_0 c^{\nu} e^{-\frac{E}{RT}} \qquad (42)$$

The solution of this non-linear system of equations in the general case encounters a great number of mathematical difficulties, which makes it necessary to solve the problems of ignition by significant simplifications. Some simplifications are reduced to studying of only stationary regimes and finding conditions when such solutions are impossible. In other simplifications, temperatures and concentrations inside the vessel are not considered and only the flow of the process in time is analyzed.

Physically, the process of self-ignition can be most clearly illustrated by the example of the simplest case. Let a certain volume of gas V be enclosed in a vessel whose walls are maintained at a given temperature T_W. Let us assume that during the reaction the temperature throughout the vessel is equal to T. In view of this, the entire temperature difference between the gas and the wall is concentrated on the boundary between the wall and the gas. Accordingly, within the vessel, in the gas, there is no difference in the concentrations of the reacting substances.

The entire volume of gas V reacts, therefore the concentrations of all components of the mixture and temperature are the same at all points, and there is no need to use the system of equations (41), (42). Instead, we can write two expressions – an expression for the rate of heat release in the entire volume V and an expression for the release of heat through the walls of the vessel.

If the thermal effect of the reaction is equal to Q *J/mol,* the rate of heat release in the vessel is:

$$q_1 = QWV.$$

As the speed W is the reaction rate (mol/m^3s), then

$$W = k_0 c^{\nu} e^{-\frac{E}{RT}}$$

And hence

$$q_1 = Qk_0 c^{\nu} V e^{-\frac{E}{RT}}. \tag{43}$$

This heat goes partly to the heating of the gas, partly through the walls of the vessel. The amount of heat lost can be represented as:

$$q_2 = \alpha S(T-T_W), \tag{44}$$

where S is the total surface of the walls of the vessel, and α is the coefficient of heat transfer from the gas to the wall.

Equation (41) is the amount of heat released as a result of the combustion reaction and is called the **heat release curve**, and equation (42) allows us to calculate the amount of heat lost to the environment through the walls of the vessel and is called the **heat removal curve.**

If $q_1>q_2$**,** the system will warm up, the temperature will increase with time, which can lead to an explosion.

If $q_1<q_2$, then, on the contrary, the system will cool down, the temperature will decrease until burning stops.

If $q_1=q_2$**,** then stationary combustion will be observed at a certain constant temperature.

Thus, the condition of stationary process means that the amount of heat released during combustion is equal to the amount of heat removed to the environment:

$$q_1=q_2,$$

that is:

$$QVk_0 n_A^{\alpha} n_B^{\beta} e^{-\frac{E}{RT}} = \alpha S(T-T_0) \qquad (45)$$

This transcendental equation (is not solved analytically) will be solved graphically.

3.2.2 Graphical solution

In order to find out under what conditions an explosion occurs, let us use a graphical construction. For the sake of further simplification, suppose that before the inflammation in the vessel, the reacting substances do not change, i.e. the concentration c is constant and equal to c_0. This assumption turns out to be quite precise in the region of weak heating of the mixture near the ignition temperature.

The system of curves q_1 in Figure 11 corresponds to the rate of heat generation for three different reaction rates (for example, for three different pressures) depending on the temperature inside the vessel (equation (43)). The straight line q_2 corresponds to the rate of heat release depending on the temperature inside the vessel, i.e. corresponds to equation (44).

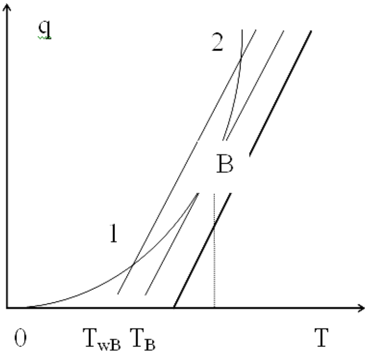

Figure 11 - Graphical solution of the system of equations (43) - (44)

When the reaction proceeds along the lower curve, first, starting with T_w, the mixture will be heated to the temperature T_1, as up to this point the heat input exceeds the heat removal. At point T_1, the heating will stop and the system will come into equilibrium. The reaction will go further at a constant rate (if in this case the number of reacting molecules does not change – we accepted it, although, in fact, the rate will start to fall progressively).

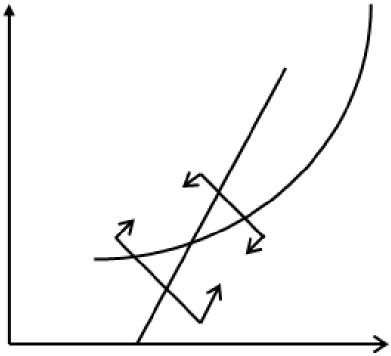

Figure 12 - Equilibrium conditions at point 1

In the case where the reaction proceeds along the upper curve, the heat release always exceeds the heat removal and, consequently, the system will continuously increase the temperature from the very beginning; the reaction rate will quickly move to very high values and lead to an explosion.

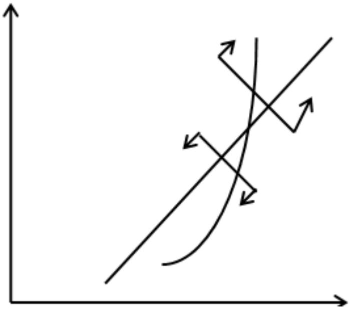

Figure 13 - Equilibrium conditions at point 2

There is, obviously, a condition characterizing the transition from the case of a limited growth of temperature to unlimited growth. This condition is realized by the mean curve for q_1. In this case, as in the first, the temperature of the gas will increase to the value T_B. From this moment, the system will be in equilibrium. What kind of balance will this be? Steady or not? To answer this question, we will examine the states corresponding to two common points of the curves $q_1(T)$ and $q_2(T)$,, which are equilibrium points. To solve our problem, we will use the usual method of studying the stability of equilibrium states of any system.

Suppose that in a system in equilibrium, some minor (more precisely, arbitrarily small) deviations from the state of equilibrium occurred, and let us study the further change in its state. At the intersection of the curves with temperature T_1 the system is in equilibrium (Figure 12).

Deviation from this point towards a lower temperature (to the left) will lead to a nonequilibrium state, in which the amount of heat q_1 released exceeds the amount of heat q_2. In this case, the system reheats and returns to the equilibrium state with temperature T_1. If the temperature is raised relative to the same equilibrium state, a nonequilibrium state occurs in which the amount of heat removed is greater than the amount of heat released, hence the system will cool and return to equilibrium again.

Thus, in both cases, randomly occurring temperature deviations create conditions for the system to return to equilibrium. Consequently, *the steady-state regime 1 is* ***stable***.

Let us now consider point 2. A similar analysis of Figure 13 shows that if $T<T_1$, then $q_1<q_2$ and consequently the system cools down and goes to point 1. If $T>T_1$, then $q_1>q_2$ and the system warms up and an explosion occurs. Consequently, *the stationary mode 2 is* ***unstable*** and therefore in practice this equilibrium state is not realized.

3.2.3. Critical ignition conditions

The state with the temperature T_B is also an equilibrium state, but it is one-sidedly stable (Figure 14): when the temperature of the system is accidentally lowered, it returns to the equilibrium state, and when the temperature increases, its unlimited increase will occur for $T > T_B$ $q_1 > q_2$ and there will be a progressive warm-up of the system. Thus, the equilibrium at the T_B temperature is *one-sidedly stable*.

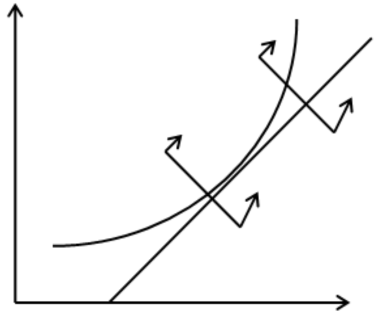

Figure 14 - Equilibrium conditions at the point of ignition B

This phenomenon is the transition from a slow quasistationary reaction accompanied by a slight heating to a rapid, nonstationary, progressively accelerating temperature increase and burning out of the mixture (as a result of the increase in temperature, the reaction rate, i.e., the intensity of heat release increases, which again leads to a temperature rise, etc. until the mixture is completely burnt out) and it was termed a "***thermal explosion***".

The boundary steady-state mode of touching the curves for releasing and removing heat (point B) is commonly referred to as the ***ignition mode***, and the corresponding temperature T_B is the ***self-ignition temperature*** or simply the ***ignition temperature***. The condition to which the state at point B corresponds is usually called the "***critical ignition condition***," since the regime at point B is characterized by a sharp, critical change in the state with an infinitesimal change in temperature.

In point B equalities $q_1 = q_2$ and $\frac{dq_1}{dT} = \frac{dq_2}{dT}$ unambiguously determine the value of T_B, which characterizes the limiting ignition condition for the given mixture.

In the example considered, the value of T_W was kept unchanged but the combustible properties of the system changed, which depend on the content of the fuel in the mixture, i.e. on the pressure and relative concentration of substances. It turned out that at a given temperature of the vessel walls, only after reaching a certain reaction intensity (a certain fuel content, a certain pressure), a spontaneous increase in temperature and a rapid acceleration of the reaction, i.e. ignition may occur.

Usually in the experiments, the composition of the mixture and the pressure are predetermined, and the variable temperature is the temperature of the walls of the vessel T_W. If we change T_W, then on the graph this will correspond to the parallel translation of the straight line $q_2(T)$. The heat dissipation curve q_1 is given. With a gradual increase in the wall temperature from the value T_{W1}, the corresponding straight line of heat transfer moves parallel to itself to the right (the value of x is considered constant).

As long as the straight line of heat removal crosses the heat input curve, the system's heating is stationary. The last temperature of the vessel wall, at which only the stationary heating takes place, is the temperature T_W. The corresponding heating temperature of the system is T_B. With a slight further increase in the temperature of the vessel wall above T_W. stationary heating is no longer possible; as the heat input always exceeds the heat removal: the system, as in the previously considered case, progressively warms up, reacts and comes to ignition.

bviously, all other wall temperatures above T_W will also lead to ignition. The value T_W thus separates the temperature region of the wall , in which no ignition occurs, from the heating region in which ignition occurs.

Unlike the self-ignition temperature, the temperature of the stationary heating of the system above which the system is capable of self-accelerating of the reaction is the ***ignition temperature***, i.e. it is the lowest temperature of the vessel walls at which an explosion occurs under the given conditions and for the given . In the examples considered, this temperature is the temperature of the vessel T_W. It is obvious that T_W. and T_B differ to a greater or lesser extent from each other, but always $T_B > T_W$.

It should be noted that in the strict (in the original sense) determination of the self-ignition temperature, it is not a constant characterizing the gas system, but it more or less depends on the experimental situation, especially, on the size of the vessel.. This follows from equation (44), where $q_2$depends on the values of S and x, characterizing the parameters of the experimental setup.

3.2.4 Induction ignition period

In practice, one way or another, it is necessary to connect the combustible properties of the substance with some characteristics of inflammation. The measurement of T_B is, mostly, an experimentally difficult task, because of the high rate of change in the temperature T inside the vessel and general difficulties of accurate measuring of gas temperatures.

Therefore, we use not the value of T_B, but the value of T_W, i.e. possibly minimum temperature of the vessel wall (in the case of forced ignition, the minimum temperature of the igniter). This quantity is connected with the other experimentally observed quantity: the ***induction period*** or the ***ignition delay***, since the transition from a given temperature T_W to a T_B temperature is always associated with a certain time needed for the development of reactions and heat accumulation.

The rate of increase in temperature and, correspondingly, the increase in the reaction rate should be proportional to the difference $q_1 - q_2$. According to equations (43) and (44):

$$q_1 - q_2 = QVk_0c^{\nu}e^{-\frac{E}{RT}} - \alpha S(T - T_W).$$

If the heat capacity of the system $c_\upsilon V$, then:

$$\frac{dT}{dt} = \frac{Q}{c_\upsilon}k_0c^{\nu}e^{-\frac{E}{RT}} - \frac{\alpha S}{c_\upsilon V}(T - T_W),$$

where c^{ν} is a function of time. It is a difficult and unnecessary task to solve this equation. In order to qualitatively represent the behavior of the temperature inside the vessel in time, we can use the above graphs $q_1(T)$ and $q_2(T)$, making the difference q_1 and q_1 for each point and identifying it with the temperature rise rate. This is given in Figure 15. The lower curve corresponds to the case of stationary heating up to temperature T_1, ignition is absent; the dotted curve corresponds to a more real case when the fuel is spent (decrease in c).

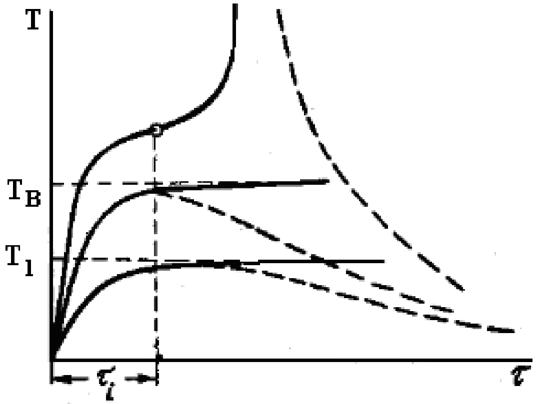

Figure 15 – An increase in temperature T of the reacting mixture with time τ; τ_i is the induction period

The curve with the designation T_B is the limiting state at the boundary of ignition. As T_W increases, this curve becomes an upper-type curve. The latter is characterized by the presence of an inflection point, after which a very rapid temperature jump (ignition) occurs. *The time corresponding to the inflection point, in this case, is analogous to the induction period in the chain development of the reaction, and can be called the* ***delay time*** *or the* ***induction period of thermal ignition.***

The higher the temperature of the walls of the vessel is raised over the T_W (connected with T_B), the less will, obviously, be the delay time. From this point of view, for the value of T_W, characterizing the flammability of the system, it would be necessary to take a value for which the delay time equals infinity. Such a strict definition of T_W is usually not made, but there are T_W values corresponding to this or that time delay. In the practice of measurements, they reach some tens of seconds for some substances and decrease very rapidly with increasing temperature; they also depend on a number of other factors (pressure, etc.).

Thus, we see that if we use the temperature of the vessel walls as the value of the ignition temperature, it is also necessary to give the value of the induction period.

3.2.5 Self-ignition boundaries

The above graphs $q_1(T)$ and $q_2(T)$ show that for a given experimental condition for each combustible mixture characterized by a certain initial composition and pressure, there is a definite value of T_B. This means that there exists an entire system of limiting states that determine the regions where the explosion can occur and where the explosion does not occur. The boundaries of such regions are called ***explosive boundaries, explosive limits*** or, more precisely, ***self-ignition boundaries.***

Let us consider the simplest quantitative relationships that enable us to establish the boundaries of self-ignition. If the system of curves $q_1(T)$ corresponds to the reaction rates at different pressures, then from the touching condition it is easy to obtain a connection between p and T corresponding to the interface between the explosion region and the region of non-explosiveness.

Taking into account that at the tangent point

$$q_1\big|_{T_B} = q_2\big|_{T_B} \qquad \text{и} \qquad \left(\frac{\partial q_1}{\partial T}\right)_{T_B} = \left(\frac{\partial q_2}{\partial T}\right)_{T_B}$$

and using (43) for q_1 and (44) for q_2, we get:

$$QVk_0c^{\nu}e^{-\frac{E}{RT}} - \alpha S(T - T_W) \tag{46}$$

$$c^{\nu}\frac{E}{RT_B^2}QVe^{-\frac{E}{RT}} = \alpha S \tag{47}$$

Dividing the first equation to the second we get the following relation:

$$\frac{RT_B^2}{E} = T_B - T_w, \qquad (48)$$

whence, rewriting this quadratic equation in the form:

$$T_B^2 - \frac{E}{R} T_B + \frac{E}{R} T_w = 0$$

It is not difficult to get T_B:

$$T_B = \frac{E}{2R} \pm \sqrt{\left(\frac{E}{2R}\right)^2 - \frac{ET_w}{R}}. \qquad (49)$$

In this expression, one should take a minus before the radical, which gives the smallest value of T_B, since the plus sign gives a meaninglessly high value (it corresponds to the tangent point of the curves q_1 and q_2 beyond the inflection point).

Thus,

$$T_B = \frac{E}{2R}\left(1 - \sqrt{1 - 4\frac{RT_w}{E}}\right). \qquad (50)$$

From this N.N. Semenov's formula it follows, in particular, that the phenomenon of ignition in the considered problem of thermal explosion can exist only in a limited range of values of the wall temperature:

$$0 \le T_w \le \frac{E}{4R}$$

The maximum value of the ignition temperature from (45) for $T_W = \frac{E}{4R}$ is

$$T_{B\max} = \frac{E}{2R}, \qquad T_{B\max} = 2T_w$$

and corresponds to the inflection point in Fig. 7 and is equal to ($5 \cdot 10^3 \div 10^4$) *K*.

In all theoretically unlimited range of values of the wall temperature above $T_{W\max} = \frac{E}{4R}$ under any heat transfer conditions, there is a "thermal explosion" region, i.e. the area in which the steady-state reaction is impossible. This follows from the fact that equation (50) has no solution, and hence there are no tangent points for the curves q_1 and q_2.

Usually $E \approx 16 \cdot 10^4$ J/*mol*, $T \approx 500 \div 1000$ *K*, therefore $4\frac{RT_w}{E} \approx \frac{32 \cdot 1000}{16 \cdot 10^4} \approx 0{,}2$ – this is a small quantity; hence, formula (50) can be given in a simpler, more approximate form, expanding the radicand in a series:

$$T_B \approx \frac{E}{2R} - \frac{E}{2R}\left(1 - \frac{2RT_{0B}}{E} - \frac{2R^2T_{0B}^2}{E^2} - \ldots\right)$$

The first approximation gives:

$$T_B \approx \frac{E}{2R} - \frac{E}{2R} + T_{0B} + \frac{RT_{0B}^2}{E}.$$

Or

$$T_B - T_{0B} \approx \frac{RT_{0B}^2}{E}$$

The expression obtained shows that the numerical value of T_B differs little from T_{0B}, if E is sufficiently large. For example, at E = 50000 J/mol and T = 1000 K, the difference

$$T_B - T_{0B} \approx 40\ \text{K}$$

This interesting and important circumstance shows that the use of an approximate T_{0B} instead of T_B in some cases does not entail a too high error.

N.N. Semenov established a relationship between the temperature and the pressure of the mixture in the state of ignition. To obtain it, let us substitute expression (48) into equation (41):

$$QVk_0 c^{\nu} e^{-\frac{E}{RT_{0B}\left(1+\frac{RT_{0B}}{E}\right)}} = \alpha S \frac{RT_{0B}^2}{E}$$

As $\frac{RT_{0B}}{E} \prec\prec 1$, approximately

$$QVk_0 c^{\nu} e^{-\frac{E}{RT_{0B}}} = \alpha S \frac{RT_{0B}^2}{E}.$$

$$\frac{EQVk_0}{\alpha SR} e^{-\frac{E}{RT_{0B}}} = \frac{T_{0B}^2}{c^{\nu}} = \left(\frac{c^{\nu}}{T_{0B}^2} \right)^{-1}$$

Taking a logarithm we get:

$$\ln \frac{EQVk_0}{\alpha SR} - \frac{E}{RT_{0B}} = -\ln \left(\frac{c^{\nu}}{T_{0B}^2} \right).$$

$$\ln \frac{EQVk_0}{\alpha SR} = \frac{E}{RT_{0B}} - \ln \left(\frac{c^{\nu}}{T_{0B}^2} \right)$$

In particular, for a bimolecular reaction $c^2 \sim p$, and

$$\ln \frac{p_k}{T_{0B}^2} = \frac{E}{2RT_{0B}} + const$$

Where p_K denotes the pressure corresponding to the critical ignition condition. This Semenov’s relation establishes a connection between T_{0B} and p_K at the boundary. According to this relation, there must be a linear relation between $\ln \frac{p_k}{T_{0B}^2}$ and $\frac{1}{T_{0B}}$ (a straight line in the coordinate system $\frac{1}{T_{0B}}$ and p_K). In the usual coordinate system of p_K and T_{0B}, this dependence gives a curve that limits the explosion area (Figure 16). This curve gives a connection between T_{0B} and $p_к$ for a given constant initial state of the mixture (c_0 = const).

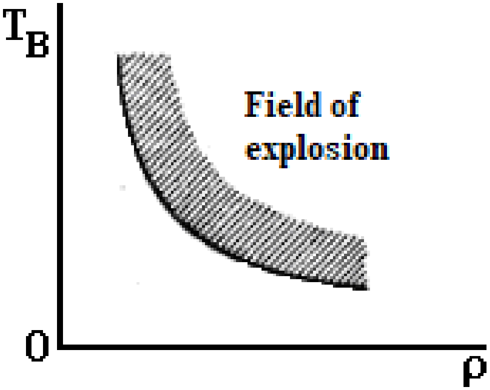

Figure 16 - Relationship between the ignition temperature and pressure for a given initial mixture composition

In the case of constant pressure (p = const), the nature of the dependence of T_B on the composition of the mixture for the bimolecular reaction according to (49) will have the form shown in Fig. 17 as a temperature dependence of the percentage of fuel. It can be seen that for p = const, not every mixture is capable of ignition, but only mixtures located in certain boundaries, for example, between the values of c1 and c2, which are called the ***concentration limits of self-ignition.***

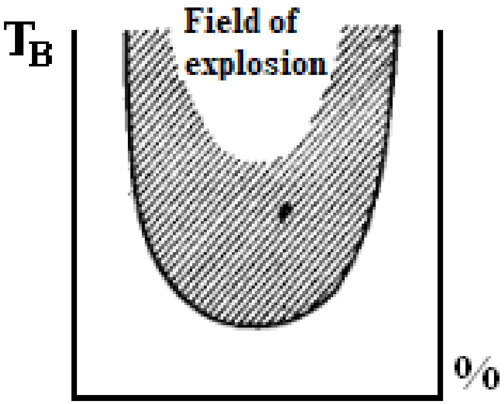

Figure 17 - Dependence of the ignition temperature on the percentage composition of the mixture at constant pressure

In addition to these two dependences of T_B on p_k and T_B on the composition of the mixture, the third type of dependence is of practical interest, it is the dependence of p_k on the composition of the mixture at a given constant value T_B (practically - T_{0B}, as $T_B \approx T_{0B}$). This dependence can be constructed on the basis of the last two figures. In this case, the contour of the ignition region will have the form shown in Fig. 18.

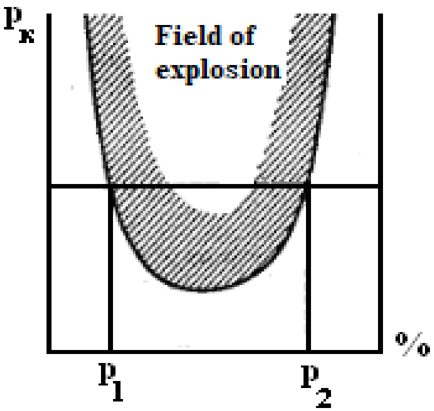

Figure 18 - Dependence of pressure, corresponding to ignition conditions on the percentage composition of the mixture at a constant T_B value

From Figure 18 it can be seen that for a given pressure, not every mixture is also capable of ignition. In particular, it can be seen that under these heat removal conditions, there is such a minimum pressure (or wall temperature $T_B \approx T_{0B}$) at which a mixture of any composition cannot self-ignite.

Thus, for any method of representing critical (limiting) conditions, there are definite and clearly outlined regions in which thermal self-ignition of gas mixtures is possible.

Thus, we have discussed in detail the problem of the heat explosion according to Semenov. A number of simplifying assumptions were adopted. One of them was reduced to the fact that the combustible mixture at all points in the volume of the vessel was heated equally, that is, the temperature of the mixture in all places of the vessel was the same at any given moment in time. However, this is not a realistic assumption, since it is clear that the layers of the mixture adjacent to the walls of the vessel will warm faster than others and the temperature in the vessel will be different in different places. Therefore, we should consider the problem of thermal explosion taking into account spatial distribution of temperature.

Test questions:

1 What are the two types of ignition?

2 What is self-ignition?

3 Write down the expression for the heat release curve and the heat removal curve.

4 What is a thermal explosion?

5 Draw diagrammatically on the chart the mutual location of the heat release and heat removal curves:

a) for stationary combustion,
b) for nonstationary combustion,
c) for critical conditions

6 What is called the delay time or the induction period of thermal ignition?

3.3 Stationary theory of thermal explosion

In the preceding chapter, the general form of the thermal ignition condition was obtained by approximate methods. Now we will consider this problem analytically in order to obtain concrete numerical results. To do this, it is necessary to solve the problem of the stationary distribution of temperatures in the system where the chemical reaction proceeds.

The theory of thermal explosion, proposed by Semenov and used as the basis for all further work in this field, is constructed in the assumption that the temperature can be assumed to be the same at all points of the explosive vessel. This concept of "homogeneous ignition" does not agree with the experimental facts; it is well known that ignition always begins at a point, and then the flame spreads through the vessel. As Todes correctly pointed out, the idea of the temperature equality in the pre-explosion period at all points of the vessel is correct only at such intensity of convection, at which the entire temperature gradient falls on the walls of the vessel. In this case the limit of thermal ignition must substantially depend on the thickness and material of the wall, which can be observed only for liquid explosives with strong artificial mixing.

On the contrary, if we assume that the heat transfer inside the gas is purely conductive, then we get a temperature distribution in the gas mixture inside the vessel with the highest temperature in the center of the vessel, where the ignition should begin. The heat transfer coefficient and the critical ignition condition will be determined by this temperature distribution: ignition should occur under conditions when the stationary temperature distribution becomes impossible, which similar to the case of thermal breakdown of dielectrics considered by Fock. In this form the problem was first posed by Todes and Kontorova, but as they wanted to get an extremely generalized form of the solution, the formulas derived by them cannot be applied to numerical calculations as well as they do not enable scientists to make qualitative conclusions.

The only concrete conclusion that has been drawn in that work is the correct relationship between the critical ignition pressure and the diameter of the vessel, which, however, can easily be obtained without an analytical solution from dimensional considerations. We will solve the problem by using the following three assumptions:

1) We assume that the pre-explosion heating is small in comparison with the absolute wall temperature: $\frac{\Delta \mathrm{T}}{\mathrm{T}} \prec\prec 1$.

2) The reaction rate will be considered to depend only on the temperature $e^{-E/RT}$, that is, we ignore the burnout of the initial substances, the dependence of the pre-exponential factor on temperature, the change in density in different parts of the vessel, etc.

3) The thermal conductivity of the wall will be assumed to be infinitely large.

The first assumption, as will be shown below, is equivalent to the condition $RT \prec\prec E$ and, thus, states a completely defined boundary of applicability of the theory.

We will see below that there is a close connection between the first assumption and the second: both of them are justified for sufficiently large values of the parameter B introduced above. With the decrease in this parameter, the correction for burning out during the induction period first becomes important, and then (for the first-order reaction for $B \prec\prec 4$)) the critical condition disappears.

The conditions for correctness of the third assumption will also be considered below in connection with the effect of external heat insulation. Here we neglect external thermal insulation, that is, assume that the initial explosion temperature T_0 is given on the inner surface of the wall.

Let us first consider the case when convection is completely absent. The heat conductivity equation for the stationary case and for a field with continuously distributed heat sources of density QW, where Q is the heat effect, and W is the rate of reaction, has the form:

$$a\Delta \mathrm{T} = -\frac{Q}{c_p \rho} W(T) , \qquad (51)$$

where a is thermal conductivity of the gas mixture; c_p is its heat capacity, ρ is the density; Δ is Laplace operator. According to assumption 3, we assume that the reaction rate $W = ze^{-E/RT}$, where E is the activation energy; and taking that $c_p \rho a = \lambda$, the thermal conductivity of the gas mixture, equation (51) can be rewritten in the form

$$\Delta\mathrm{T} = -\frac{Q}{\lambda} z e^{-\frac{E}{RT}} . \tag{52}$$

We must solve this equation in the boundary conditions given on the walls of the vessel: on the basis of Assumption 3, we can specify a constant temperature T_0 on the inner surface of the walls.

The solution of equation (52) satisfying the boundary conditions will give a stationary temperature distribution in the reaction vessel at wall temperature. At a certain temperature such a distribution becomes impossible; we will consider this temperature as the ignition temperature. Its connection to the thermal effect and the reaction rate, the thermal conductivity of the mixture, the shape and dimensions of the vessel can be found from an analysis of the properties of equation (52) and its solutions. Derivation of this connection will be our task.

As we showed in the previous chapter with the help of the similarity theory, the desired stationary temperature distribution must contain one dimensionless parameter δ. Now our task is to find a specific analytic form of this distribution. For an infinite vessel with plane-parallel walls, equation (51) can be integrated in a general form for any law of the dependence of the reaction rate *W* on temperature. In this case, it takes the form:

$$\frac{d^2T}{dx^2} = -\frac{Q}{\lambda} W(T) . \tag{53}$$

The general integral of this equation for any form of the function *W (T)* is taken by two quadratures and has the form:

$$x = \int \frac{dT}{\sqrt{-2\int \frac{Q}{\lambda} W(T)\,dT}}$$

with two arbitrary constants. The critical condition of ignition will be a set of values of parameters at which this expression cannot satisfy the boundary conditions for any values of arbitrary constants. If we put the origin of coordinates in the middle of the vessel and denote its width through $2r$, the boundary conditions are formulated as follows: for $x = \pm r$; $T = T_0$. Because of symmetry, it is possible to solve the equation for half of the vessel, in the combined boundary conditions:

for $x = r$; $T = T_0$; for $x = 0$, $\frac{dT}{dx} = 0$. In order to find the criterion for fulfillment of the boundary conditions, we set the temperature in the middle of the vessel T_m as a parameter and solve the equation in the Cauchy conditions: for $x = 0$, $T = T_m$ and $\frac{dT}{dx} = 0$ then the equation takes the form:

$$x = \int_{T}^{T_m} \frac{dT}{\sqrt{2\int_{T}^{T_m} \frac{Q}{\lambda} W(T)\,dT}}. \qquad (54)$$

It contains one variable parameter T_m determined from the boundary condition:

$$r = \int_{T_0}^{T_m} \frac{dT}{\sqrt{2\int_{T}^{T_m} \frac{Q}{\lambda} W(T)dT}} \qquad (55)$$

The second arbitrary constant in (54) is absent because the form of the solution (54) automatically satisfies the second boundary condition for $x = 0,\ \frac{dT}{dx} = 0$.

Let us denote the integral on the right-hand side of (55) by $\psi(T_m, T_0)$.T0). If this integral is a monotonic function of T_m, then a stationary regime is always possible.

If the form of the function *W (T)* is such that, with variation of *Tm*, ψ passes through an extremum, then this extremum must give a critical ignition condition. It gives directly the critical size of the vessel; with dimensions lying on the other side of the extremum, condition (55) cannot be satisfied for any value of *Tm*. It is physically obvious that the critical size of the vessel must be maximum, and the considered extremum is a maximum.

The most general form of the critical ignition condition for a plane-parallel vessel is, therefore:

$$\left(\frac{\partial \psi}{\partial T_m}\right)_{T_0} = 0 . \qquad (56)$$

At values of *r* greater than critical, it is impossible to get a stationary temperature distribution in the vessel. At *r* values less than the critical value, it is geometrically obvious that each *r* value must correspond to at least two values of *Tm*, that is, two different stationary temperature distributions in the vessel. In the elementary Semenov’s theory, this corresponds to two intersections of the direct heat removal curve with a reaction velocity curve, which degenerate at the limit to the tangent point. From the analogy with Semenov's theory, we conclude that only one of the two possible stationary temperature distributions can be stable, which corresponds to a smaller value of *Tm*.

The stationary distribution is formally obtained for any value of the temperature in the middle of the vessel. But not all these distributions are stable.

Let us consider the real form of the dependence of the rate of reaction on temperature. The substitution of the Arrhenius law into Eqs. (53) - (56) leads to an expression that is not integrated in elementary functions and is very inconvenient for computations. After this equation (53) takes the form (for $\vartheta = T - T_0$):

$$\frac{d^2\vartheta}{dx^2} = -\frac{Q}{\lambda} z e^{-\frac{E}{RT_0}} e^{\frac{E}{RT_0^2}\vartheta}, \tag{57}$$

or in dimensionless variables $\theta = \frac{E}{RT_0^2}\vartheta; \quad \xi = \frac{x}{r}$, where r is the half-width of the vessel:

$$\frac{d^2\theta}{d\xi^2} = -\delta e^{\theta}, \tag{58}$$

and δ has the value

$$\delta = \frac{E}{RT_0^2}\frac{Q}{\lambda}r^2 z e^{-\frac{E}{RT_0}} . \tag{59}$$

The general integral of equation (58) has the form:

$$e^{\theta} = \frac{a}{ch^2\left(b \pm \sqrt{\frac{a\delta}{2}} \cdot \xi\right)} \tag{60}$$

with two arbitrary constants *a* and *b*. By the symmetry condition $\left(\frac{d\theta}{d\xi}\right)_{\xi=0}$ or $\theta(\xi) = \theta(-\xi)$, the constant *b* must be zero (this is the condition of equality of the temperatures of both walls of the vessel), and the integral takes the form:

$$e^{\theta} = \frac{a}{ch\left(\sqrt{\frac{a\delta}{2}} \cdot \xi\right)} . \tag{61}$$

An arbitrary constant *a* is determined from the boundary condition for $\xi = 1 \; \theta = 0$, from which we obtain the transcendental equation for the determination of *a*

$$a = ch^2\sqrt{\frac{a\delta}{2}} . \tag{62}$$

For the values of δ, for which (62) has a solution, it is possible to get a stationary temperature distribution, the form of which can be found by substituting this solution in (61). For the values of δ, for which (62) does not have a solution, an explosion will occur. The critical ignition condition is determined by the value of δ, for which (62) does not have a solution. For the following presentation it is convenient to introduce, instead of the integration constant a, a new quantity σ connected with it by the relation

$$a = ch^2\sigma .$$

Then the transcendental equation (62) takes the form:

$$\frac{ch\sigma}{\sigma} = \left(\frac{\delta}{2}\right)^{-\frac{1}{2}} . \qquad (63)$$

Now it is easy to see that the critical ignition condition is determined by the minimum value of the quantity $ch\sigma/\sigma$; this minimum is obtained for $\sigma_{\kappa p} = 1{,}2$ and gives

$$\sigma_{\kappa p} = 088 \qquad (64)$$

as a critical condition of ignition.

We can find the maximum pre-explosive heating from (61) for

$$\xi = 0 :$$

$$\theta_m = \ln a_{\kappa p} = \ln ch^2\sigma_{\kappa p} = 1{,}2 , \qquad (65)$$

$$(\Delta \mathrm{T})_m = 1{,}2\frac{RT_0^2}{E} . \qquad (66)$$

Thus, the problem of self-ignition for a plane-parallel vessel is completely solved.

The analytic expression (61) enables us to consider also the stationary temperature distribution when the reaction occurs in a vessel under the explosive limit. If we denote the value of the dimensionless temperature θ at the center of the vessel by θ_0, equation (61) is rewritten as

$$\theta = \theta - 2\ln ch\sigma\xi \, , \qquad (67)$$

where

$$\theta_0 = 2\ln ch\sigma \, . \qquad (68)$$

The quantity σ is a function of the parameter δ expressing the combination of all the properties of the system (the velocity and the thermal effect of the reaction, the thermal conductivity, the dimensions of the vessel) determined from the transcendental equation (63). The solution of this equation is shown in Fig. 19, and only a part of the curve up to the maximum corresponds to stable temperature distributions. At the value of σ=1.2, corresponding to the maximum, an explosion occurs. Smaller δ values correspond to smaller *Tm* values and, consequently, as it was said above, to stable steady-state temperature distributions, large σ- values correspond to unstable temperature distributions.

If all the properties of the mixture, the experimental conditions and the dimensions of the vessel are known, we can calculate the value of parameter δ. If this value is greater than 0.88, then a stationary temperature distribution is impossible – an explosion should occur. If the value is less than 0.88, then according to the curve (Figure 19) we find the corresponding value of *a* (the smaller of two possible values), and from it and equation (68) we can determine heating in the middle of the vessel and from equation (67) – distribution of temperatures throughout the vessel.

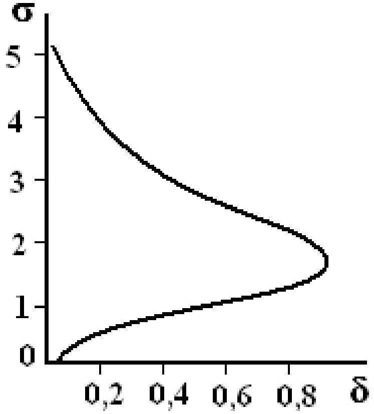

Figure 19 - Solution of the transcendental equation (63)

Now we have to find the critical value and magnitude of pre-explosive heating for vessels of spherical and cylindrical shape. For these cases, the equation for temperature takes the form: for an infinitely long cylindrical vessel:

$$\frac{d^2\theta}{d\xi^2} + \frac{1}{\xi}\frac{d\theta}{d\xi} = -\delta e^{\theta}; \qquad (69)$$

For a spherical vessel:

$$\frac{d^2\theta}{d\xi^2} + \frac{2}{\xi}\frac{d\theta}{d\xi} = -\delta e^{\theta}$$

Here $\xi = \frac{x}{r}$ where r is the radius of the vessel. The boundary conditions have the form: for $\xi = 1$, $\theta = 0$; for $\xi = 0$, $\frac{d\theta}{d\xi} = 0$

Test questions:

1 What assumptions were made in the stationary Frank-Kamenetsky's theory?

2 Write down the general form of the critical ignition condition for a plane-parallel vessel.

3 How to find the critical value of δ?

4 What is the form of the temperature equation for an infinitely long cylindrical vessel?

5 What is the form of the temperature equation for a spherical vessel?

4 NORMAL COMBUSTION OF LAMINAR FLAMES

4.1 Waves of chemical reaction

Any well-mixed mixture of fuel and oxidizer from a chemical point of view contains everything necessary for combustion. However, under normal conditions (atmospheric pressure and room temperature) the rate of chemical reaction in most combustible mixtures is very low, it takes centuries to see any chemical transformations in them. When considering the phenomena of chain and thermal ignition, we saw that the combustible mixture ignites only under certain conditions, it is necessary either to warm up the walls of the vessel, or to introduce an igniter from the active centers.

Let us imagine that these conditions are realized not throughout the reaction vessel, but somewhere in one place, for example, a heated wire or spark created a local warming up of the combustible mixture, or a rather large number of active centers is obtained by photoinitiation. After a local initiation, a reaction wave will occur, which will gradually cover the entire reactive mixture.

Two different modes of propagation of the reaction wave in space are known: with supersonic and subsonic velocities. The first – detonation – is caused by a rapid compression of matter in the shock wave, which provides the required heating of the substance in order for the reaction to proceed at a considerable speed; in turn, the release of heat in a chemical reaction maintains a constant intensity of the shock wave and thus provides its spread over long distances. The second mode of propagation of the chemical reaction wave occurs with velocities much lower than the sound velocity, and is associated with the molecular processes of thermal conductivity and diffusion – this is the mode of flame propagation.

In the thermal mechanism of flame propagation, the heat released during the chemical reaction is transferred to the neighboring sections of the unreacted gas, heats them and initiates an active chemical reaction. In the chain mechanism, the propagation of the reaction site occurs through the diffusion of active sites. A combined action of diffusion and thermal conductivity is also possible and most likely in real cases of combustion.

Experimental data and theoretical considerations indicate that when the flame propagates, the reaction occurs at each instant of time in a comparatively thin layer (in comparison with the dimensions of the combustion chambers), the reaction zone. In the immediate vicinity of the reaction zone, also in a thin layer, the unburned mixture is heated. Therefore, in the first approximation, the flame propagation can be imagined as follows: there are two regions – the unburned gas and reaction products separated by a combustion surface, whose thickness can be neglected and treated as a geometric surface moving with respect to the gas with a known velocity – the normal velocity of flame propagation.

The normal flame velocity determines the volume of the combustible mixture, which burns per unit time per unit flame surface; it has the dimension of linear velocity (cm/sec). In the curved flame front, the normal (or fundamental) burning rate characterizes the velocity of the flame front relative to the initial mixture in the direction normal to the surface of the front.

The value of the normal velocity of flame propagation is determined by the kinetics of the chemical reaction and by the molecular processes of heat and material transport inside the flame front characterized by large gradients of temperature, concentrations of substances participating in the combustion reaction, velocity and density.

In practice, the calculation of the normal flame velocity is often complicated by the fact that the kinetics of the chemical transformation is poorly known or completely unknown. Therefore, when solving gasodynamic combustion problems, the value of the normal flame velocity is taken not from a theoretical calculation, but from the experimental data. The measurement of the normal flame velocity in the experiment is not particularly complicated, several methods have been developed for such measurements in a wide range of pressure, composition, and temperature changes.

When analyzing the phenomena occurring at the surface of the flame, it is often convenient to choose a local coordinate system associated with the flame front (in which the flame surface is swept); in this coordinate system, the initial combustible mixture with a velocity of u_n flows onto the fixed front of the flame, and the combustion products flow away from the flame surface with a velocity ub, larger than u_n, as during combustion, the gas is heated and expanded. It is obvious that the rate of inleakage u_n, at which the front of the flame is at rest, is equal to the speed at which the flame moves relative to the stationary gas. The quantity u_b is the velocity of the flame moving in space in the situation when the combustion products are at rest. The relationship between the values of u_n and u_b of a plane flame front can be found as follows; the total mass of matter entering the flame per unit surface of the front must be equal to the mass of the combustion products removed from this surface, i.e.

$$\rho_0 u_n = \rho_b u_b \tag{70}$$

where ρ_0 and ρ_b are densities of the initial mixture and combustion products.

Hence

$$\frac{u_b}{u_n} = \frac{\rho_0}{\rho_b} = \frac{\mu_0}{\mu_b}\frac{T_b}{T_0}, \tag{71}$$

where T_0 and T_b, μ_0 and μ_b are temperature and average molecular weight of the initial mixture and combustion products (the pressure in the propagating flame is almost constant in the volume of the gas, and we will see that its change is proportional to the square of the Mach number). As for ordinary combustion reactions $\mu_0 \approx \mu_b$, and the temperature during combustion varies by a factor of 5-10, $u_b / u_n \approx 5 \div 10$.

According to the law of conservation of the mass flow through the flame front (70), it is also convenient to use the concept of the mass combustion rate $p_0 u_n$, which is the product of the gas density per velocity. This value has the dimension of g/cm^3-s and represents the mass of matter burning in one second per 1 cm^2 of flame. Similarly, the rate of heat release during combustion can be considered per unit of the flame surface; the corresponding value has the dimension of cal/cm^2- s.

This chapter presents physical foundations of the theory of thermal flame propagation, which is the foundation of modern ideas about the laws governing propagation of waves of chemical transformation.

4.2 Chemical transformation in flame

Let us consider the transition from the initial state of the cold combustible mixture to the final combustion product in the flame, the width of the transition zone and the time spent by the reacting substance in it.

From the general considerations it can be foreseen that the chemical reaction inside the flame front will proceed in nonuniformly, because of the sharp dependence of the reaction rate on temperature, it will be mainly concentrated in the part of the flame front adjacent to the hot combustion products. In the places where the temperature is lower, the reaction proceeds at a much lower rate, and therefore it can be neglected, and consider only the molecular transfer of heat and matter. These processes in the flame dominate because of the large temperature gradient and large concentrations of reacting substances, and they mainly determine the structure of the flame.

Let us first, determine the order of the size of the zone, which is called the heating zone.

Hertz solved the problem of a thermal wave ahead of a heated surface moving at a constant velocity. This solution, which was first applied to the flame by V.A. Mikhelson, who considered the reaction zone as a surface $x = 0$ with a fixed temperature T_b,

$$T = T_0 + (T_b - T_0)e^{u_n x/\chi}, \qquad (72)$$

where T_0 is the temperature of the unperturbed substance, u_n *is* the speed of the flame (the velocity of its surface relative to the fresh gas), and $\chi = \lambda / \rho c_p$ is the coefficient of thermal diffusivity, the ratio of thermal conductivity to density and heat capacity at constant pressure. The thermal wave is considered here in the coordinate system associated with the flame front

a fresh combustible mixture moves into the flame from the side of negative x with a velocity of u_n (see Fig. 20). For simplicity, in (72) and in (73) all material constants ρ, λ, χ are considered constant, independent of temperature. In combustion, this assumption is violated strongly, for example, χ changes 10-30 times. Further in this section, this assumption is not used.

The distribution (72) is a solution of the heat conductivity equation

$$\rho u c \frac{dT}{dx} = \lambda \frac{d^2T}{dx^2} \qquad (\lambda,\ c = const), \qquad (73)$$

satisfying the boundary conditions $T(\infty) = T_0$, $T(0)=T_ъ$. The solution (72) is applicable only to the region $x<0$, in which there is no heat release, for $x>0$ there are combustion products of a constant temperature $T_ъ$ (see Fig. 20). It can be seen from (72) that as the scale of the width of the heating zone we can take the distance at which the heating grows *e* times:

$$l = \frac{\chi}{u_n} = \frac{\lambda}{\rho c u_n}. \tag{74}$$

Let us calculate this value for a slowly burning mixture (6% of methane with air), for which u_n = 5 cm/s, and a rapidly burning explosive mixture of stoichiometric composition with u_n = 103 cm/s. Substituting $\chi \approx 0{,}3\,\text{cm}^2$/s, we obtain $l = 0.06$ cm (CH_4), $l \approx 0.0003$ cm ($2H_2 + O_2$).

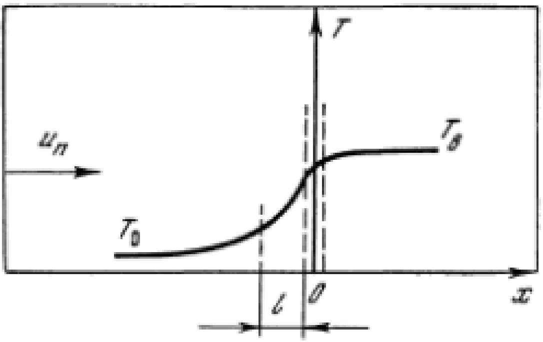

Figure 20 – Michelsol’s temperature distribution in the flame front: l is the width of the heating zone, the dashed line shows the reaction zone, x <0 - unburned gas, x> 0 are the products of combustion

In both cases, the width of the heating zone is many times greater than the mean free path of the gas molecules, which is natural, since the velocity u_n is much smaller than the speed of sound; indeed, from the kinetic theory it follows that

$$\chi \sim \Lambda c_s \tag{75}$$

(Λ is the mean free path, c_s is the thermal velocity of the molecules, which is of the order of the speed of sound) and, consequently,

$$l \sim \frac{\Lambda c_s}{u_n} \succ\succ \Lambda . \tag{76}$$

This inequality is a justification of the applicability of the differential equations of molecular transport (thermal conductivity and diffusion), which are used in the theory of flame propagation.

The order of the residence time of the substance in the flame can be obtained by dividing the width of the heating zone by the flame velocity: $t_n = 4 \cdot 10^{-3}$ s (CH_4), $t_n = 10^{-7}$ s ($2H_2$+O_2).

The time of the chemical reaction is of the same order as the residence time of the reacting mixture in the heating zone. This time is many times greater than the mean free path of the molecules in the gas: any reaction in the flame, because of a large heat of activation or a complex mechanism, requires a large average number of molecular collisions per one effective collision leading to transformation.

Let us emphasize once again that the temperature and composition of the mixture in the flame change not only as a result of a chemical reaction. They also change in the zone where there is no chemical reaction – in the heating zone. The temperature varies due to the thermal conductivity of the gas, and the composition changes due to diffusion. The chemical reaction in the flame proceeds in the mixture that has already undergone heating and whose composition has already changed.

Take, for example, a mixture of carbon monoxide with oxygen, reacting as $2CO + O_2 = 2CO_2$. Not taking into account the complex mechanism of this reaction, we will depict qualitatively the temperature distributions, concentrations of carbon monoxide, oxygen and carbon dioxide in the flame front (Fig. 21).

The initial mixture is heated by the heat flow from the reaction zone. The composition of the mixture in the heating zone varies as compared to the initial mixture due to the diffusion of reagents into the reaction zone and its dilution by the combustion products (CO_2). In combustible mixtures with reagents sharply different in molecular weights, the relative content of the oxidant and fuel also changes, as the more mobile molecules of the light reagent diffuse at a higher rate

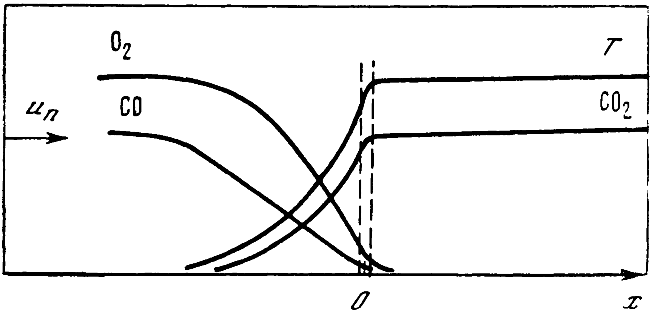

Figure 21 - Structure of the flame front, in which the reaction $2CO+O_2=2CO_2$ proceeds.

Concentrations of CO and O_2 in the reaction zone are much lower than their initial values; however, the increase in temperature compensates the corresponding decrease in the reaction rate, so that the basic chemical transformation occurs in a narrow zone near the maximum temperature, the temperature of the flame. Diffusion continuously delivers the reacting substances to the reaction zone and redistributes them in the reaction zone. The completion of the reaction in the combustion wave occurs, as a rule, asymptotically (in combustion products, in the region where diffusion flows are practically zero, a thermodynamic equilibrium corresponding to the initial composition of the mixture and the combustion temperature is established).

A specific feature of the reaction kinetics in the flame is the absence of all delaying stages in the reaction. During self-ignition the stage of accumulation of heat and (or) active centers hampers the development of the process, whereas there are no such slow processes in the flame. In the temperature range, in which heating of the mixture due to heat release in the chemical reaction would be slow, the flow from the neighboring gas layers causes a rapid rise in temperature; similarly, active centers diffuse from *a* into the layer.

However, we should note that it is not easy to understand this basic process for the theory of combustion. Let, for example, some combustible mixture give a burning temperature of 2000 K, and a noticeable reaction occurs in the range of 1700-2000 K. By increasing the initial temperature, we increase the burning temperature to 3000 K; we will say that the reaction now occurs in the temperature range, say, 2300-3000 K, and at a temperature below 2300 K it can be neglected. The question arises: why did we in the mixture with a combustion temperature of 3000 K neglect the chemical reaction at 1700-2000 K, which we previously considered (for a mixture with a combustion temperature of 2000 K) fast?

The answer to this question is as follows. A higher combustion temperature, without decreasing the reaction rate at 1700-2000 K, provides a much higher reaction rate near the combustion temperature. Due to this, the speed of flame propagation and time, during which the temperature varies from 1700 to

2000 K, sharply decreases. In a slowly burning mixture (with a combustion temperature of 2000 K), this is enough time for the entire combustible mixture to react; in the fast-burning mixture, the residence time of the mixture in the temperature range 1700-2000 K is reduced to such a degree that only a small part of the mixture reacts at such temperatures; the flame velocity corresponds to a reaction proceeding at a higher rate at temperatures of 2300-3000 K.

This significant factor was not taken into account in the first theories of thermal flame propagation, in which a fixed ignition temperature T_i was introduced as a certain physical constant of the combustible mixture and it was assumed that the rate of chemical reaction at $T>T_i$ was constant. Therefore, these theories lead to erroneous statements regarding the effect of the reaction kinetics on the velocity of flame propagation.

4.3 Similarity in the distribution of temperature and concentration in the flame

The structure of a laminar flame is described by a system of heat conduction and diffusion equations. Let us consider the simplest case when the front of the flame is flat, and the chemical reaction is described by a single stoichiometric equation. In the coordinate system moving along with the flame front, the equations have the form

$$\frac{d}{dx}J_T = QW(a_i, T), \tag{77}$$

$$\frac{d}{dx}J_i = -\frac{\nu_i}{\nu_1}W(a_i, T), \tag{78}$$

(the change in the heat flux J_T and the fluxes of reactants J_i is due to heat release and changes in the quantities of reactants in the chemical reaction). Here Q is the heat of the reaction, and a_i denote the relative weight concentrations of reagents; the rate of the chemical reaction is calculated per mole of the substance to which index 1 is assigned. We will assume that there is insufficient amount of this substance in the initial mixture.

<u>The flows of heat and matter consist of convective and molecular transfer</u>

$$J_T = -\lambda \frac{dT}{dx} + \rho u c T\,, \tag{79}$$

$$J_i = -\rho D_i \frac{da_i}{dx} + \rho u a_i\,, \tag{80}$$

where D_i are the diffusion coefficients, c is the specific heat at constant pressure.

Taking into account the equation of continuity of the mass flow in $\rho u = \rho_0 u_n = \rho_b u_b = const$, the system of equations (77) - (80) can be rewritten in the form

$$\rho u c \frac{dT}{dx} = \frac{d}{dx} \lambda \frac{dT}{dx} + QW(a_i, T)\,, \tag{81}$$

$$\rho u \frac{da_i}{dx} = \frac{d}{dx} \rho D_i \frac{da_i}{dx} - \frac{\nu_i}{\nu_1} W(a_i, T)\,. \tag{82}$$

Let us now consider a mixture of gases of similar molecular weight. In this case, the diffusion coefficients can be considered equal. In addition, if the potentials of intermolecular forces between different molecules are not very different, it follows from the kinetic theory that the diffusion coefficients are approximately equal to the coefficient of temperature conductivity of the gas mixture in the entire temperature range

$$D_i \approx \chi \ \ (\lambda \approx \rho c D_i) \,. \tag{83}$$

In such mixtures, the cross-effects of molecular heat and mass transfer (thermal diffusion, diffusion thermal conductivity, etc.), which we did not take into account when writing the fluxes in (79) and (80), are also insignificant.

For illustration, let us give the values of the coefficients of thermal conductivity and the product $\rho c D$ for oxygen and hydrogen at room temperature: thermal conductivity of O_2 is 5.9 10^{-5}, of H_2 – 407.10^{-5}; the product $\rho c D$ for the diffusion of O_2 in N_2 is 5.8 10^{-5}, diffusion of H_2 in $O_2$is 23 10^{-5}, for H_2 in N_2 – 21 10^{-5}, for H_2 in H_2-38 10^{-5} cal/cm s grad.

With equal diffusion coefficients of the reacting substances and in the presence of a single-stage chemical reaction, their concentrations are related to each other by simple linear relations

$$\frac{a_{i0} - a_i}{\nu_i} = \frac{a_{j0} - a_j}{\nu_j} \,, \tag{84}$$

which are fulfilled at any point in space. Here, the concentration of chemical components in the initial fuel mixture is denoted with an index 0.

Indeed, if the diffusion equation from system (82), including the concentration a_i, is multiplied by $1/\nu_i$, and the diffusion equation for a_j is multiplied by $1/\nu_j$, and we subtract one from the other, then we obtain a linear diffusion equation (without the chemical reaction rate function) for a linear combination of concentrations $(a_i/\nu_i) - (a_j/\nu_j)$, whose solution, bounded on the entire segment of the *x*-axis, is $(a_i/\nu_i)-(a_j/\nu_j)=const$. If the constant is determined from the conditions for the initial fuel mixture, we obtain (84).

Relations (84) allow us to calculate the distribution of concentrations of reagents if the distribution of the concentration of one of them, for example a_1, is known. Therefore, the basic system of equations (81), (82) can be represented as two equations (we omit the subscript 1)

$$\rho uc\frac{dT}{dx}=\frac{d}{dx}\lambda\frac{dT}{dx}+QW(a,T), \tag{85}$$

$$\rho u\frac{da}{dx}=\frac{d}{dx}\rho D\frac{da}{dx}-QW(a,T), \tag{86}$$

in which the reaction rate by means of (84) is presented as a function of only one reactant and temperature.

We note here that a linear relationship between any two concentrations of reacting substances with equal diffusion coefficients was obtained using the notion that the entire chemical transformation takes place in a single chemical reaction. If the process occurs in such a way that there are several zones of chemical transformation separated from each other, as often happens in the propagation of a flame with chain combustion reactions, then the relations (84) are not satisfied everywhere.

However, using a complex kinetic combustion mechanism, for the same diffusion coefficients and thermal diffusivity, one can obtain a linear relationship between all concentrations and temperature, expressing the law of conservation of the total energy of the system in space. More details about this relationship will be given considering flames in the systems with chain reactions.

The simplest ariant such a relationship is obtained if we have only one active substance, on the concentration of which the rate of the chemical reaction depends, as in the case of system (85), (86).

Multiplying the diffusion equation (86) by a constant value of Q , adding it to the heat conductivity equation, and taking into account the equality $\chi = D$, we obtain the equation for the total enthalpy of the gas H

$$\rho u \frac{dH}{dx} = \frac{d}{dx}\frac{\lambda}{c}\frac{dH}{dx}, \qquad H = Qa + \int_0^T c dT , \qquad (87)$$

which does not include the rate of chemical reaction. The total enthalpy of the system is the sum of the thermal and chemical energy at constant pressure per unit mass of the gas (the kinetic energy of the gases is small compared with the heat content, and it is not taken into account). The only bounded solution of equation (87) for all x is

$$H = const, \qquad (88)$$

where the constant can be determined from the conditions in the initial combustible mixture:

$$const = H_0 = Qa_0 + \int_0^{T_0} c dT . \qquad (89)$$

Thus, although thermal energy and chemical energy individually vary in space, their sum remains constant. The increase in the thermal component of energy when the mixture is heated is compensated by the decrease in chemical energy, which is caused by diffusion from this zone of reacting substances-carriers of chemical energy.

The assertion that the sum of the chemical and thermal energy inside the flame is constant was expressed as a hypothesis in 1934 by Lyss and Elbe for the case of the chain reaction initiated by the diffusion of active centers. Let the flame velocity be determined by very light active centers, the concentration of which is very small; then neither diffusion nor thermal conductivity noticeably changes the concentration and temperature fields. In this case, the reaction proceeds as in a vessel with a movable piston (pressure is constant), and the enthalpy conservation is obvious. However, as shown above, the constancy of the total enthalpy in a stationary flow does not depend on the mechanism of the reaction, but on the relationship between the diffusion coefficients and the thermal conductivity of the mixture.

We recall that the total enthalpies of the initial mixture and products are equal to each other for any relations between χ and D , which is the law of energy conservation. But if, in addition, the condition $\chi = D$ is satisfied, and the conversion rates of the reacting substances are related by stoichiometric relationships (a simple reaction), then the total enthalpy is constant inside the flame.

For a constant heat capacity, the constancy of the total enthalpy inside the flame can be written in the form

$$Qa + cT = Qa_0 + cT_0 = cT_b, \qquad (90)$$

that is, the temperature and concentration distributions turn out to be similar

$$\frac{a_0 - a}{a_0} = \frac{T - T_0}{T_b - T_0}. \qquad (91)$$

Similarly, the distribution of temperature and the distribution of concentrations of the other reacting substances (a_1 is linearly related to a_i , see (84)), and also concentrations of the combustion products are similar, if, of course, their diffusion coefficients are also equal χ. Similarity also occurs in those cases when the rate of a simple reaction depends on the concentrations of the final products of the reaction (reversible reaction or autocatalysis by the final product). If the reaction is complex, concentrations of the intermediate products are not related by stoichiometric relationships, and there is no similarity of the fields. But even in this case, when all the transfer coefficients are equal $(D_i = \chi)$, the total enthalpy of the system also remains constant $\mathrm{H} = const$, but from this one cannot obtain an unambiguous dependence $a_i = f(T)$ for each of the substances participating in the reaction.

The simplest case, when the propagation of a flame is described by the system of equations (85), (86) and all the conclusions derived from it are valid, is the case when the reacting substance. This situation often arises when the flame propagates in combustible mixtures, the composition of which differs sharply from stoichiometric. The reaction rate in such mixtures is limited by the concentration of one substance, which is not sufficient, and then, when the diffusion coefficient of this substance is equal to the thermal diffusivity coefficient, there is a similarity of fields of its concentration and temperature. This missing component can be called the carrier of chemical energy; the final temperature of the mixture, which is reached during combustion, depends on its concentration.

From the law of energy conservation

$$H_0 = Qa_0 + \int_0^{T_0} cdT = \int_0^{T_b} cdT \qquad (92)$$

it follows that the final temperature of the combustion products is determined only by the initial heat content of the combustible mixture (the thermal effect, the initial concentration of the missing reagent and the initial temperature), and the average heat capacity of the mixture at constant pressure. For a constant heat capacity

$$T_b = T_0 + \frac{Qa_0}{c}\,. \tag{93}$$

(We note once again that relations (92) and (93) hold for any χ and *D.)*

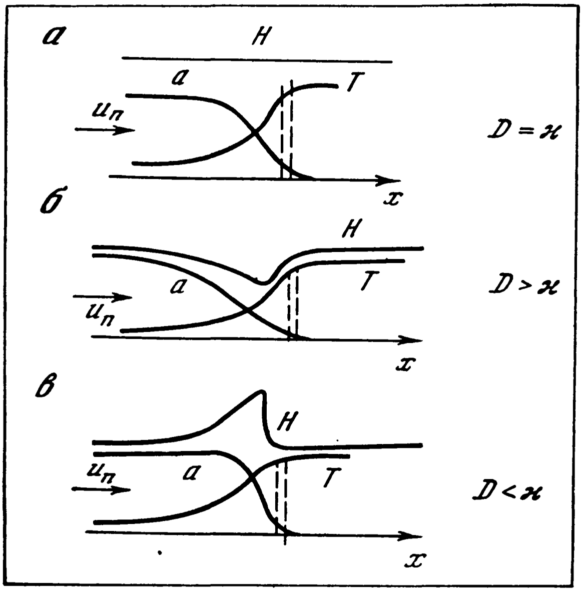

Figure 22 - Distribution of the reacting substance, temperature and total enthalpy in the flame front for various ratios between the diffusion and thermal conductivity coefficients

For $D \neq \chi$ inside the flame, the amount of chemical and thermal energy is not conserved, but from general considerations, one can predict in which direction the deviations will occur. Thus, in a poor mixture of hydrogen and air, the coefficient of diffusion of hydrogen – the carrier of chemical energy – is an order of magnitude greater than the thermal diffusivity of the mixture; therefore, diffusion removes hydrogen more intensively from the gas layer in the heating zone than when the gas is heated by molecular thermal conductivity. As a result, in the case of a hydrogen-air mixture (i.e., at $D \succ \chi$), the total enthalpy in the heating zone has a minimum.

On the contrary, in a lean mixture of a high molecular weight hydrocarbon, for example benzene with air, the thermal conductivity is greater than the diffusion coefficient of benzene vapor ($\chi \succ D$), and heating of the mixture in the heating zone is more intensive than the removal of benzene by diffusion to the reaction zone; therefore the total enthalpy has its maximum in the heating zone. For illustration, Figures 1.28, *a, b, c* show the distributions of the concentration of the reacting substance, temperature and total enthalpy in the flame for various ratios between the diffusion coefficients and thermal conductivity.

Further we will encounter a situation in which there is a similarity, or in a more general case, connection of concentration and temperature fields. When certain conditions are fulfilled, this situation also arises in nonstationary combustion, in combustion in complex hydrodynamic fields, and in nonplanar flame fronts.

Similarity can also be maintained if the rate of the chemical reaction clearly depends on the coordinate and time. Let us give an example. Let a catalyst, causing a rapid reaction at the initial temperature, be introduced into a region $x_1<x<x_2$ of the space occupied by the combustible mixture for a time t, $t_1 \prec t \prec t_2$, which leads to heating and subsequent ignition and propagation of the flame.

A more complicated is the case when the energy is introduced into a combustible mixture at a certain time and place from outside (using an electric spark or focused laser radiation). Then the equation for the total enthalpy becomes nonstationary and a new function $\Phi\ (x,\ t)$ appears in its right-hand side, depending on the coordinate and time, which describes the action of the external energy source.

Knowing the solution of this equation $H\ (x,\ t)$, we can express the concentration a as a function of temperature, coordinate and time, $a = a\ (T,\ x,\ t)$ and, consequently, get $W\ (a,\ T) = W\ [a\ (T,\ x,\ t),\ T] = W\ (T,\ x,\ t)$. Now the problem again reduces to solving one heat equation instead of two, but the reaction rate function W obviously depends on T, x and t (and not only on temperature, as in the problem without the external source.) Nevertheless, the solution of the problem of ignition by an external source for $\chi = D$ is substantially simplified.

4.4 Formula for the normal flame propagation velocity

The linear relationship between concentration and temperature, obtained in the previous section for the case of equality of diffusion coefficients and thermal conductivity, enables us to pass from the system of two differential equations for balance of combustible substance and energy to one equation. To do this, it is sufficient to express the concentration in terms of temperature for the rate of the chemical reaction and to represent the reaction rate $W\ (a,\ T)$ as a function of only temperature $W\ [a\ (T),\ T] = W\ (T)$. Therefore, we can consider one energy equation

$$\rho u c \frac{dT}{dx} = \frac{d}{dx} \lambda \frac{dT}{dx} + W(T) \qquad (94)$$

It is very important that that in this second-order equation, the parameter includes the mass burning velocity ρu, which will also be determined as a result of solving the problem.

A special chapter is devoted to a detailed mathematical study of the problem of thermal propagation of flame and determination of the normal flame velocity as an eigenvalue of the problem. In this section, we will only discuss the basic physical concepts of the structure of the flame, which will allow us to obtain an approximate formula for the flame velocity.

In the flame, a rapid chemical reaction occurs in a narrow temperature range adjacent to the burning temperature. The heat released in the chemical reaction is used primarily to heat the nonreacting mixture from the initial temperature to the temperature of the reaction zone (see Fig. 20).

In the narrow zone of the chemical reaction, the temperature derivative changes from the final value on the side of the reacting mixture - from the zone of the chemical reaction, the heat is transferred to the heating zone by heat conduction - to zero from the combustion products, where thermal and chemical equilibrium is achieved. A rapid change in the derivative of temperature over a short space gap means a large contribution of thermal conductivity. Due to this, in the reaction zone, the contribution of convective heat flux variation (in the reaction zone the temperature difference is small) in comparison with the contribution of thermal conductivity can be neglected in the heat equation. Thus, in the reaction zone, we can consider the "truncated" equation

$$\frac{d}{dx}\lambda\frac{dT}{dx}+QW(T)=0 \qquad (95)$$

Equation (95) is easily integrated. Using the independent variable T and making a substitution, we have

$$\frac{d}{dx}\lambda\frac{dT}{dx} = \frac{z}{\lambda}\frac{dz}{dT} \tag{96}$$

and, consequently, the order of equation (95) decreases; it becomes

$$z\frac{dz}{dT} + \lambda QW(T) = 0\,. \tag{97}$$

In the products of the reaction $a = 0$, the temperature is constant and equal to the burning temperature T_b, so we can set the boundary condition

$$T = T_b\,,\ \lambda\frac{dT}{dx} = z = 0\,. \tag{98}$$

Integrating (97) from the current temperature T to T_b (heat conductivity can be considered constant over the reaction zone $\lambda = \lambda_b = const$), we obtain a heat flux from the reaction zone to the heating zone

$$\lambda_b\frac{dT}{dx}\Big|_{T_b} = \sqrt{2\lambda_b Q\int_T^{T_b} W dT}. \tag{99}$$

Integration in (99) can be extended to the initial temperature: at low temperatures the rate of the chemical reaction is negligibly small, so that over the low-temperature region the integral in (99) can be considered equal to zero. The heat release function will contribute to the integral only at high temperatures, by order of magnitude, the actual region of integration is equal to the characteristic temperature interval (in the case of the Arrhenius heat-release function). We recall that the function *W (T)* includes the dependence on the concentration *a (T) м*, therefore $W(T_b) = 0$.

The amount of heat released in a chemical reaction per unit time and diverted by thermal conductivity is equal to the reserve of chemical energy that carries the flow of the hot mixture (in our coordinate system the flame is at rest and the combustible mixture moves at a rate equal to the normal propagation velocity of flame). Therefore, we can write

$$\sqrt{2\kappa_b Q \int_{T_0}^{T_b} W(T)dT} = \rho_0 u_n Q a_0 \, . \tag{100}$$

From this equation we get the formula for the normal velocity of propagation of a laminar flame

$$u_n = \frac{1}{\rho_0 a_0} \sqrt{\frac{2\lambda_b}{Q} \int_{T_0}^{T_b} W(T)dT} \, . \tag{101}$$

Formula (101) shows that the flame velocity depends on the integral of the heat release function and, thus, is related to the order of the chemical reaction, its activation energy, and other kinetic and physical-chemical characteristics of the combustible mixture.

4.5 Relationship between the combustion rate and the kinetic properties of gases

Let us return to the discussion of the formula for the flame velocity (101). As the function *W* depends strongly on temperature, as a rule, according to the Arrhenius law, the order of magnitude of the integral in (101) can be estimated as the product of the maximum value of *W*, which we denote by *Wmax*, the effective width of the temperature interval, which for the Arrhenius dependence is $\theta = RT_b^2 / E$. Thus, we get

$$u_n \approx \frac{\sqrt{2\lambda_b Q W_{\max}\theta}}{\rho_0 c\left(T_b - T_0\right)}. \tag{102}$$

Let us determine the average reaction time t_r as the time over which at the maximum rate of heat release all the heat contained in the initial mixture will be released – the reaction heat goes on heating of the fuel mixture from T_0 to T_b, From the equation of the thermal balance

$$Q W_{\max} t_r = \rho_0 c\left(T_b - T_0\right) \tag{103}$$

We find W_{max} and substitute it into (102). Then

$$u_n \approx \sqrt{\frac{2\lambda_b\theta}{\rho_0 c\left(T_b - T_0\right)}\frac{1}{t_r}} = const\sqrt{\frac{\chi_c}{t_r}}$$

$$\left(const = \sqrt{\frac{2\theta}{T_b - T_0}}\right). \tag{104}$$

We should note that the relation $u_n \sim \sqrt{\chi_b / t_r}$ also follows from the analysis of dimensions. As the flame velocity is determined by the characteristic time of the chemical reaction t_r and the molecular heat transfer (thermal conductivity of the mixture χ), it must be connected with them by the equation (104).

Let us analyze how the rate of flame propagation is related to the kinetic properties of the gas.

Substituting in (104) the expression for thermal conductivity (75) into the ratio of the velocity of flame to the speed of sound, we find

$$\frac{u_n}{c_s} \sim \sqrt{\frac{\chi_b}{c_s^2 t_r}} \sim \sqrt{\frac{\Lambda}{c_s t_r}} \sim \sqrt{\frac{t_c}{t_r}}\,, \qquad (105)$$

where $t_c \sim \Lambda / c_s$ is the mean free time of molecules. As only a small fraction of the colliding molecules enter the chemical reaction, then $t_c \prec\prec t_r$ and hence $u_n \prec\prec c_s$, the speed of the flame is much less than the speed of sound. The reaction time t_r is the product of the average number of collisions Z experienced during this time by a molecule capable of reacting (i.e., an oxidizer or a fuel molecule), and the average time between two collisions

$$t_r = Z \frac{\Lambda}{c_s}\,. \qquad (106)$$

Substituting this dependence in (105), we find for the flame velocity is

$$u_n \sim c_s / \sqrt{Z} \tag{107}$$

and the characteristic width of the flame is

$$l \sim \Lambda\sqrt{Z}\ . \tag{108}$$

The relation (107) is the Einstein expression for the average diffusion velocity in a certain direction, in which *Z* is the total number of collisions experienced by the particle during the diffusion time, and (108) is the Einstein expression of the mean path traveled by the molecule for Z free paths. The reason for this becomes clear, if we turn to the molecular pattern of flame propagation: the fuel molecule experiences Z collisions in the combustion zone; during this time it passes the path *l* with the average speed u_n.

A significant difference between the diffusion process and the process of flame propagation is that the average velocity of the diffusing particles decreases with time (as $1/\sqrt{t}$), whereas the flame velocity is constant in time. During combustion, the movement of the flame is connected with the displacement of molecules not along the entire path traveled by the flame front: each molecule passes within the combustion zone only a very short section of its path, experiencing an average of *Z* collisions, after which, reacting, creates conditions necessary to provide the next molecule to pass a similar path, etc.

This process can be compared to a relay race. The athlete, running at a maximum speed a small distance, passes the relay to the next, etc., as a result of the relay passes any arbitrarily large distance with a large constant speed. The ordinary diffusion in this description can be compared to long distance runners, who, starting running at maximum speed, have to slow down their run when they are tired.

4.6 Some conclusions from the formula for the velocity of flame propagation

The basic formula (101) enables us to determine the influence of various physical-chemical parameters of the mixture (pressure, temperature, composition of the mixture, order of the reaction, etc.) on the propagation velocity of the flame.

At first glance, it may seem surprising that the calorific value of the mixture Q in the expression for the flame velocity contains a denominator. Indeed, it is known from practice that with increasing calorific value the flame speed increases. The paradox is explained by the fact that an increase in Q also causes an increase in the combustion temperature (in fact, Q enters not only in the denominator (101)); and the increase in the integral of the reaction rate overlaps the increase in Q in the denominator.

In the unpublished experiments of P.Ya. Sadravnikov, made at the Institute of Chemical Physics of the USSR Academy of Sciences, the burning rates of explosive mixtures of carbon monoxide with air diluted by combustion products were compared; the diluted mixtures were preheated, so that their combustion temperature did not differ from the combustion temperature of the undiluted mixture. These experiments with satisfactory precision confirmed the relation following from the theory $Q\rho_0 u_n = const$ for $T_b = const$.

The initial concentration of fuel enters (101) not only in the denominator before the root; with increasing a_0, T_b increases and $W(T)$ increases in the region of integration.

Let us now consider how the rate of propagation of the flame changes with pressure. As the density is proportional to the pressure, and the reaction rate depends on the pressure according to the power law P^n (n is the order of the reaction), then from formula (101) we obtain

$$u_n \sim \mathrm{P}^{\frac{n}{2}-1}. \qquad (109)$$

Thus, for bimolecular reactions, the flame velocity does not depend on pressure, for trimolecular reactions it increases, and for monomolecular reactions it decreases with pressure.

In bimolecular reactions, the rate of chemical transformation is determined by the number of double collisions between reacting molecules that does not depend on pressure: the free path and the mean free time are inversely proportional to pressure, while the velocity of the molecules does not depend on pressure.

According to (107), for a constant average number of collisions necessary for the reaction the velocity u_n is proportional to c_s, and therefore it is also not a function of P. Moreover, it can be asserted that the process of flame propagation, in which the chemical transformation, including any arbitrary number of bimolecular reactions, proceeds, remains similar to itself when the pressure changes: as the pressure increases, all spatial scales (the size of the heating zones and the chemical reaction) and the time scale (the mean free time of molecules, the time of the chemical reaction) decrease proportionally to $1/P$; whereas the number of collisions, the velocity of the thermal motion of the molecules, and the velocity of propagation of the flame do not change. It should be noted that the similarity of flames in which bimolecular reactions occur is not a consequence of any particular formula for u_n, but is the most common property that follows from molecular kinetics.

Similarity is violated in the case of monomolecular and trimolecular reactions, for which it is necessary to take into account the characteristic decay time of the molecule and the existence of metastable chemical complexes. In this case, the only characteristic velocity – velocity of the molecules remains, and the flame velocity is equal to the velocity of the molecules multiplied by the dimensionless function, which depends on the dimensionless ratio of the gas-dynamic cross section characterizing the transport processes to the cross section of the chemical reactions, which now depends on P.

It should be kept in mind that besides direct influence on the rate of chemical reaction in the flame, the pressure can affect the flame propagation velocity through the combustion temperature of the mixture. It is caused by the dissociation of combustion products, which becomes significant in hot flames. Trimolecular reactions play an important role in dissociation equilibrium; this is why the change in pressure affects the dissociation and, consequently, the combustion temperature, which strongly affects the flame propagation velocity. With increasing pressure, dissociation in combustion products is suppressed (the rate of trimolecular reactions of recombination processes increases) in comparison with bimolecular dissociation, which leads to an increase in the combustion temperature and the flame propagation velocity.

We considered the linear velocity of flame propagation, while the mass burning velocity p_0u_n, as all available experimental data show, always increases with pressure. As $p_0u_a \sim P^{n/2}$, this means that in accordance with the presented ideas, the reaction rate, as it is expected, increases with pressure.

According to numerous experimental data, the dependence of u_n on P varies from $u_n{\sim}P^{-0,5}$ ($\rho_0 u_n{\sim}P^{-0,5}$) for slowly burning mixtures (hydrocarbons) to $u_n{\sim}P^{0,5}$ ($\rho_0 u_n{\sim}P^{1,5}$) for fast burning systems (rich mixtures of carbon monoxide with oxygen, hydrogen-oxygen mixtures).

In some early experimental works (see [79]), an anomalous dependence of $u_n(P)$ in the mixture of $CO + O_2$ was found: the mass velocity of the flame decreased with increasing pressure. These observations were made in the analysis of experiments carried out at different pressures, but at the same partial pressure of water. As it was explained later, water vapor significantly accelerates the oxidation reaction of carbon monoxide. The increase in total pressure at a constant, partial pressure of water vapor was equivalent to a decrease in water content in the fuel mixture; caused by this circumstance, the decrease in velocity is stronger than the increase in velocity due to the increase in pressure.

For the overwhelming majority of combustion reactions, unfortunately, there are no reliable kinetic schemes, especially at high temperatures. Therefore it is interesting to use the experiments with flames as kinetic experiments: using formula (101) for the burning rate, we can make a conclusion about kinetic characteristics of combustion reactions.

Thus, from the dependence of the flame velocity on the pressure, one can obtain the data on the total order of the chemical reaction in the flame. It is convenient to represent the experimental data on the graph in the coordinates lg u_n, lg P, the slope of the experimental curves in this graph, is linearly related to the order of the chemical reaction – the tangents to them determine the so-called baric coefficient of flame propagation velocity

$$\beta_p = \left(\partial \ln u_n / \partial \ln P\right)_{T_0}.$$

Measurement of the flame propagation velocity at different combustion temperatures can be used to determine the total activation energy of the chemical reaction in the flame. Indeed, from formula (102) it follows that for the Arrhenius dependence of the reaction rate on the temperature, the flame propagation velocity u_n and the burning temperature $T_ь$ are connected by the following relation:

$$u_n \sim \exp(—E/2RT_{ь}) \qquad (110)$$

If the results of the experiments are plotted on the graph in the coordinates ln u_n, $1/T_{ь}$, then the slope of the curve can be used to calculate the temperature coefficient of the flame propagation velocity $\beta_p = \left(\partial \ln u_n / \partial \ln T_0\right)_p$ and the effective activation energy in the flame.

4.7 Limits of the combustion spread

It is known from the experience that in flammable mixtures strongly diluted with inert gases, the flame does not spread. At first glance it seems that this fact contradicts the theory in which it is shown that $u_n \sim \exp(—E/2RT_{ь})$, and therefore the dilution of the mixture should only lead to a decrease in the flame velocity, but not to the cessation of the whole combustion process. However, this is not observed in the experiments – combustible mixtures burn only if the content of fuel and oxidizer is sufficient for combustion at a speed of not less than a few centimeters per second.

As the dilution increases, u_n falls to a certain minimum value, and with further dilution, combustion becomes impossible. This circumstance was used as one of the main prerequisites in the old theories of combustion, based on the idea of the existence of a fixed ignition temperature T_i.

The concentration limits of flame propagation in these theories seemed obvious: if, as a result of the dilution of the mixture, the burning temperature $T_{ъ}$ is lower than T_i, then burning of the gas is impossible. However, the calculation of the flame velocity from these theories leads to the conclusion that the velocity of the flame should decrease smoothly with dilution, that is, with decreasing $T_{ь}$, reaching zero at $T_{ъ} = T_i$, which contradicts the experimental data. In fact, the combustion limits are caused by thermal losses to the environment and to radiation.

Some heat is transferred by the thermal conductivity through the walls of the pipe.

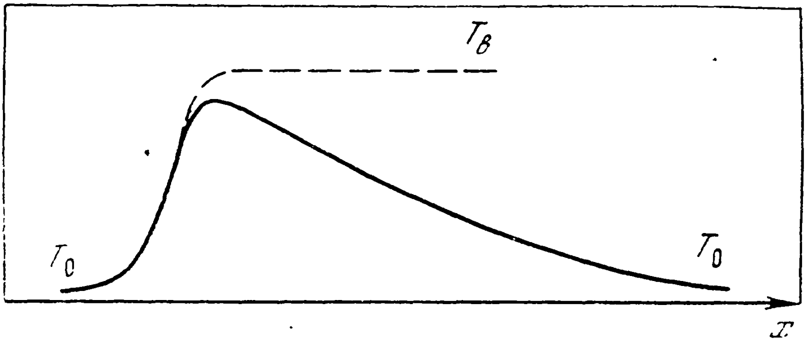

Figure 23 - Temperature distribution in the flame front with heat loss to the environment. The dotted line shows the temperature distribution without heat loss

Heat losses mainly occur in the heating zone and in the area of combustion products. Cooling leads to a decrease in the temperature at a distance from the reaction zone and appearance of a corresponding longitudinal (in the direction opposite to the propagation of the flame) heat flux (Fig. 23). The removal of heat from the reaction zone to the combustion products depends on the rate of their cooling.

For these reasons, the flame temperature T'_b under real combustion conditions of the combustible mixture turns out to be less than the adiabatic combustion temperature T_b calculated from (93), and accordingly the flame propagation velocity in the presence of thermal losses u'_n is less than the normal velocity u_n corresponding to the thermodynamic temperature T_b.

However, thermal losses through thermal conductivity to the walls and radiation, to a lesser extent, depend on the speed of flame propagation.

Let's estimate the heat fluxes from the heating zone to the walls of the pipe with which it is in contact and into the volume filled with the combustion products. The value of the first of them, related to the unit surface of the flame front, can be estimated as follows:

$$q_1 \approx \alpha\left(\frac{2\pi r_0}{\pi r_0^2}\right)\frac{\chi}{u_n'}\left(T_0' - T_0\right) = 2\frac{\alpha}{r_0}\frac{\chi}{u_n'}\left(T_b' - T_0\right) \qquad (111)$$

where α is the heat transfer coefficient, r_0 is the pipe radius. From the heat conductivity equation

$$\rho_0 u_n{}' c \frac{dT}{dx} = -\frac{2}{r_0}\alpha\left(T_b' - T_0\right), \qquad (112)$$

which describes the temperature distribution in the combustion products, we find the heat flux into the combustion products

$$q_2 = -\lambda \frac{dT}{dx}\Big|_{T=T_b'} = \frac{2}{r_0}\alpha\frac{\chi}{u_n'}\left(T_b' - T_0\right). \qquad (113)$$

It is interesting that two physically different processes have practically the same effect on the maximum temperature in the combustion zone $(q_1 = q_2)$.

The energy balance, which was in the absence of heat loss written as

$$Qa_0 = c\left(T_b - T_0\right), \qquad (114)$$

is now written as

$$\rho_0 u_n' Q a_0 = \rho_0 u_n' c\left(T_b' - T_0\right) + q_1 + q_2 \cong \rho_0 u_n' c\left(T_b' - T_0\right) + \\ + \frac{4}{r_0}\alpha\frac{\chi}{u_n'}\left(T_b' - T_0\right) \qquad (115)$$

From equations (114} and (115) we find

$$T_b' = T_b - \frac{b}{\left(u_n'\right)^2},$$

where $b = 4\alpha\chi\left(T_b - T_0\right)/\, r_0 c \rho_0$

Thus, the account for heat loss shows that the combustion temperature depends on the flame velocity: the smaller the velocity, the higher the heat transfer to the pipe walls and, consequently, the lower $T'_ь$.

The burning rate u'_n~ exp$(-E/2RT'_b]$ depends on the actual temperature reached in the reaction zone, and the lower the temperature $T'_ь$, the higher the heat removal. We assume that $T'_ь$ differs very little from Tb, therefore, the expression for u'_n can be represented in the form

$$u_n' = const e^{-\frac{E}{2RT_b}} e^{-\frac{E(T_b - T_b')}{2RT_b^2}} = u_n e^{-\frac{E(T_b - T_b')}{2RT_b^2}} \qquad (116)$$

Thus, we have obtained two relations (115) and (116) between the quantities u_n' and $T_b{}'$.

Let us represent graphically the curve $u_n'(T_b)$ from (116), which is always the same for the given mixture (curve 1 in Figure 24), and the dependence (115) under different heat transfer conditions, i.e. for different *b* (curves 2 , 3, 4).

For small *b* (curve 2) there are two points of intersection, i.e. two solutions. The lower point corresponds to an unstable, physically unrealizable regime, as on the lower branch *AB* of curve 1 an increase in the heat dissipation leads to an increase in the velocity. For sufficiently large *b* (curve 4), there is no intersection, the propagation of the flame is impossible.

For some b = b* the curves touch and the velocity u'_{n*} corresponding to the point of tangency is the limiting one.

From the conditions of tangency of curves 1 and 3, we find the critical value of *b* at which combustion becomes impossible.

$$b_* = \frac{u'_{n*} R T_b^2}{E}, \tag{117}$$

and from (115) and (116) the highest possible decrease in temperature

$$T_b - T'_{b*} = \frac{R T_b^2}{E} \tag{118}$$

and the minimal velocity

$$u'_{n*} = \frac{u_n}{\sqrt{e}} = 0{,}606 u_n \tag{119}$$

at the limit of flame propagation.

Thus, the propagation of a flame is possible only in mixtures whose burning temperature differs from the adiabatic combustion by an amount less than $RT^{2}_{ь}/E$. When the mixture is diluted, leading to $T'_{ь}$, lower than $T'_{ъ*}$ the propagation of flame is impossible.

Let us pay attention to the fact that the parameter b in the critical condition is inversely proportional to the square of the radius of the tube (the heat transfer coefficient is $a \sim 1/r_0$). The decrease in the diameter of the tube leads to an increase in the relative fraction of the heat loss, and according to the above ideas, there must exist a critical diameter at which propagation of the flame in the channel is impossible.

The phenomenon of the critical diameter was discovered by Davie in 1816 and was used for construction of a safe miner lamp. In it, a copper mesh with small holes prevents the flame from spreading from the interior of the lamp to the atmosphere of the mine, in which methane can be contained in quantities sufficient for ignition.

Expanding the dependence of the coefficient b on the diameter of the tube, we obtain the dependence of the critical diameter on the properties of the explosive mixture

$$d_* = \frac{const}{u_n P}. \tag{120}$$

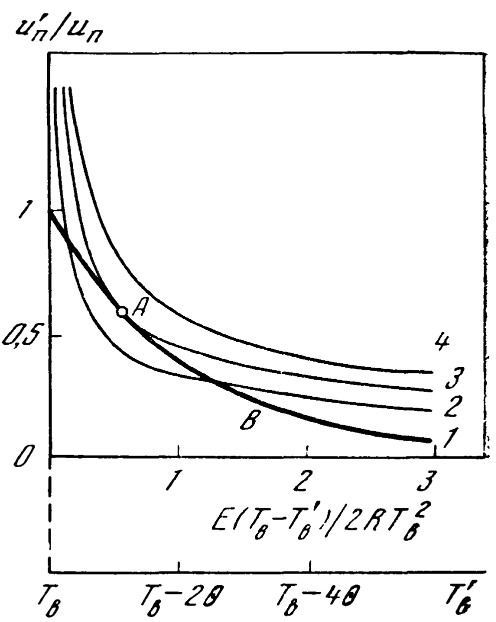

Figure 24 - Graphical solution of the system of equations (115), (116)

This dependence was confirmed by the results of experiments on combustion in narrow tubes. It may seem that from formula (120) it follows that in broad tubes, arbitrarily small flame velocities are possible. However, this conclusion contradicts the experiment, which shows that in large tubes the increase in the diameter does not lead to a decrease in the critical value of u'_{n*} and thus indicates a different mechanism of heat loss in wide tubes, different from the molecular heat conductivity.

Such a mechanism is heat emission by radiation. Estimates show that the heat losses due to conductive heat transfer to the walls of the tube are comparable to the losses of heat through radiation if the tubes are not too narrow. Thus, the calculation showed that when a ten percent mixture of carbon monoxide is burned in the air, the losses due to each of heat transfer mechanisms are comparable for a tube diameter of 5 cm; the velocity of flame propagation is 2-3 cm/s.

We should note that the losses on thermal radiation do not depend on the dimensions of the vessel, but are determined by the concentration of substances, which are able to radiate, i.e. the amount of radiation enables us to estimate the concentration limits of flame propagation.

4.8 Diffusion-thermal instability of the flame

So far, considering a laminar flame, we assumed that there exists a plane flame front propagating with a constant velocity, with a stable thermal and diffusion structure. This fact was not questioned. However, often in the experiments, the flat flame front decomposes into separate spots of combustion – so-called "cellular flames" are formed. For example, a flame torch on a Bunsen burner transforms into a pyramidal flame, sometimes even rotating around its axis, when the flame propagates in tubes, an oscillating combustion front often occurs, and so on.

These effects are often caused by the internal instability of a flat laminar flame, which does not allow it to persist for a long time. There are several reasons why the flame is unstable. Non-stability of the flame can be caused by the processes of heat conduction and diffusion, responsible for the structure of its front, and gas-dynamic perturbations in the combustible mixture and combustion products. The role of heat diffusion processes is manifested in their effect on small perturbations that affect the structure of the flame front, but do not cause significant gas-dynamic perturbations.

The region of the combustion products is shaded, solid arrows indicate the direction of the heat flows, the dotted arrows show the diffusion flow

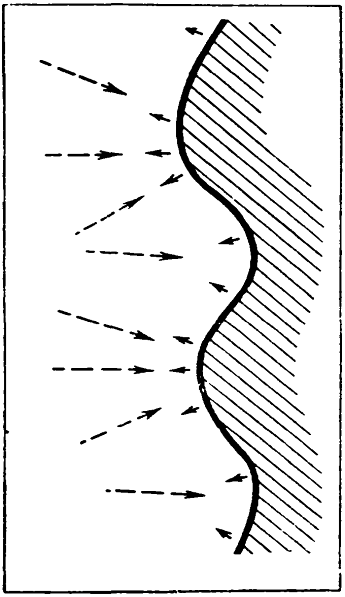

Figure 25 – Illustration of diffusion-thermal instability of the flame for $D \succ \chi$ with respect to the curvature of its front

On the contrary, gasdynamic perturbations have a large scale, far exceeding the heat diffusion width.

In 1934, B. Lewis and G. Elbe, considering the change in the total enthalpy inside the flame (see Figure 22), came to a conclusion that at a thermal diffusivity coefficient χ greater than the diffusion coefficient D, the flame must be unstable.

They explained their conclusion by the fact that with such a relation between the transfer coefficients in the heating zone, there must be a maximum of full enthalpy – the flame "absorbed" the excess energy, i.e., it came to a state in which, as a rule, the system is unstable.

However, further theoretical and experimental studies have shown that the derivation of Lewis and Elbe is not complete. For $\chi \succ D$ the flame can be unstable under certain conditions. But there is also an instability of another type, which arises with the opposite relation between the transfer coefficients. Why it appears, can be seen in Figure 25.

Consider the curved front of a laminar flame. If we study the effect of only thermal conductivity on the curvature of the flame, then it can be verified that the thermal conductivity must reduce the curvature of the flame and lead to its stabilization. Indeed, sections of the chemical reaction zone convex toward the cold fuel mixture should give off more heat than in a flat flame: heat from them is transferred not only forward in the direction of flame propagation, but also in lateral directions. Cooling of the reaction zone caused by this will lead to a lag in the forward sections of the flame. The situation will be different for concave sections, where, for the same reasons, the temperature will rise, the reaction rate will increase, and they will spread with greater speed along the flame propagation. Thus, the surface of the curved flame front will e level. In other words, the thermal conductivity has a stabilizing effect on the curved flame.

The opposite conclusion can be made if we consider the diffusion of the fuel component that limits the reaction. The convex sections of the front are in the position more favorable for the supply of combustible material than other parts of the front of the flame – they collect the hot substance from the larger volume of the combustible mixture by diffusion (see the dashed arrows in Figure 25). Due to diffusion, the reaction rate in convex sections will increase and the curvature of the front will increase even more. Diffusion, thus, has a destabilizing effect. Final

The final answer to the question about the diffusion-thermal stability of the flame depends on the relationship between the diffusion and thermal conductivity processes. For $\chi \succ D$ it is natural to expect the existence of a plane flame front, and with the reverse relation, the outward convex tongues of the flame so strongly deplete the mixture that remains in between them, that it becomes non-flammable, and the front of the flame breaks up into separate unconnected convex sections. The instability of the flame for $\chi \prec D$ with respect to the distortions of its front was established by Ya. B. Zel'dovich.

Test questions:

1 What are the two modes of propagation of the reaction wave in space?

2 What is the normal flame propagation speed?

3 What is called the reaction zone?

4 When do the temperature and concentration distributions turn out to be similar?

5 What is the total enthalpy of the reacting system?

6 Write a formula for the normal propagation velocity of a laminar flame.

7 How does the pressure of the mixture affect the flame propagation velocity?

8 What is the relationship between the combustion temperature and the speed of flame propagation?

9 What effect does the composition of the mixture have on the speed of flame propagation?

5 COMBUSTION OF A COAL PARTICLE

5.1. Heterogeneous and diffusion combustion

Let us assume that between carbon and oxygen only one combustion reaction takes place on the surface of the phase, moreover, in the first order with respect to the concentration of the reacting gas. We will also assume that the process is not accompanied by side reactions in the gaseous phase of carbon monoxide or on the surface of the coal (reduction of carbon dioxide). At the same time, it is obvious that many aspects in the combustion theory of carbon are not taken into account (penetration of the reaction into the depth of the solid phase and the region of relatively low temperatures, considered in general form for porous bodies by Zeldovich and in detail – for the combustion of coal by Khitrin, the influence of coal ashing, Frank- Kamenetsky's assumption of the fractional order of the coal reaction with oxygen).

Let us first consider general elementary concepts of the diffusion theory of heterogeneous combustion.

In accordance with the foregoing, there are two main components in the combustion process: the supply of the reacting gas to the surface of the solid phase and the flow of the chemical reaction.

The observed rate of the total combustion process in the general case will depend on the with which each of these phenomena can occur separately.

In a steady-state process, the amount of oxygen diffusing to the surface of the coal is naturally equal to its quantity burning at the reaction surface, i.e., equal to the total (observed) burning rate calculated from gas. The possible ("potential") rates of diffusion and reaction can, however, sharply differ from each other. In the case when one of them is much smaller than the other, the actual speed of the process (as well as the actual velocities of both constituent phenomena) practically coincides with the smaller possible speed of individual phenomena, which in this case plays a decisive role in the entire combustion process.

Following the generally accepted terminology proposed by D.A. Frank-Kamenetsky, we will call the combustion process "diffusion" if the diffusion rate of the reacting gas is substantially less than the possible rate under these conditions and, consequently, the unrealizable rate of chemical reaction on the surface.

The opposite limiting case of the process in which the slowest link, determining the total rate of the reaction, is the reaction rate, whereas the high rate of diffusion possible under these conditions is not realized, we call the "kinetic" combustion.

Finally, the general case of combustion – with commensurate values of the rates of diffusion and reaction (possible in the given conditions of the process) is called an "intermediate" type of the process.

These concepts of the limiting (diffusion and kinetic) burning regions and the general case (intermediate combustion region) in application to real processes are not only methodological but also practical. Actually, the conditions of combustion, the nature of the influence of individual parameters, the methods for increasing the completeness of combustion or the intensification of the process, etc., differ sharply for the diffusion and kinetic regions of combustion; they are also different in the intermediate region, with a noticeable, although not dominant, predominance of the role of one of the factors – the rate of diffusion or that of chemical reaction. Therefore, the effectiveness of any technical measures on improving the combustion process is always associated with preliminary determination of the slowest, slowing down process of the phenomenon.

The difference between diffusion and kinetic combustion is most easily traced in the example of the reaction of carbon with oxygen, although the main conclusions are applicable to other cases of the heterogeneous process (reactions on solid catalysts).

In the diffusion region of combustion, the steady-state process is determined mainly by the hydrodynamic properties of the system. In particular, according to the laws of convective diffusion, which practically coincide with the laws of convective heat transfer, the main role is played by two factors: the relative air blast velocity and the size of the coal particles. An increase in the relative velocity of air movement, as well as a reduction in particle size, leads to an intensification of the diffusion of oxygen to the surface of the coal.

As the total process in the diffusion region is limited by the rate of oxygen supply to the surface, and the possible reaction rate on the surface is much higher than the real rate (due to the lack of oxygen), the concentration of oxygen near the surface under diffusion burning is practically zero.

In the kinetic region of combustion, the hydrodynamic factors naturally do not affect the burning rate, since there is always an excess of oxygen near the coal surface: in this case there is no noticeable difference in the concentration of oxygen at the coal surface. The rate of kinetic combustion, in contrast to the rate of diffusion combustion, depends sharply exponentially on temperature. In this case, the kinetic properties of coal (the so-called "reactivity") are very important.

In general, in the intermediate combustion process, the total process is affected by all factors – hydrodynamic and kinetic; an increase in the blast velocity or grinding of particles increases the diffusion rate, brings its actual value (realized in the given conditions) closer to the possible and thus leads to a displacement of the total process toward the kinetic region. An increase in temperature in contrast to this leads to a sharp increase in the rate of the chemical reaction and a shift of the total process to the side of diffusion combustion. Naturally, the most common is the general, intermediate case of burning. One can, however, assume in general terms that diffusion combustion predominates at high temperatures, low blast velocities, and large particle sizes; on the contrary, the role of kinetic combustion is particularly great in the region of low temperatures, high values of the relative air velocity, and very small particle sizes. However, none of these factors, taken separately, determines the nature of the total process; only from the joint consideration of all of them, taking into account the kinetic properties of the fuel (high "reactive capacity" - prevalence of diffusion, low, inert fuel, kinetic region of combustion), one can make a correct conclusion on the actual nature of combustion.

Imagine a section of the coal reaction surface. Let the concentration of the reacting gas away from the surface be c_o, and on the surface itself, c, and $c_o \geq c$.

The equation of stationary thermal balance is, for simplicity of calculation, considered for the unit of reaction surface. For this purpose, we first write separately the expression for the amount of heat released per unit time per unit surface:

$$Q_1 = \alpha_Д (c_o - c) q = k_o e^{-E/RT} c \cdot q \tag{121}$$

where α_d is a quantity analogous to the coefficient of convective heat transfer a, which we will call the diffusion exchange coefficient or, briefly, the gas-recovery coefficient;

ko is the constant of the heterogeneous reaction, whose dimension for the first-order reaction (as well as the coefficient α_d) coincides with the linear velocity dimension [m/s] ',

q is the thermal effect of the reaction per unit volume of the reacting gas; the other quantities have the same values as before.

Note that for the heterogeneous process, in particular for coal, the quantities *ko* and *E* in the equation of the Arrhenius law ($k_o = k_o e^{-E/RT}$), have the meaning of the reduced, total kinetic characteristics of the reaction. We will regard them as some of the constants that are subject to experimental determination, which do not reflect the actual reaction mechanism, sometimes quite complex.

For the reaction of carbon combustion, the results of a significant number of experimental studies were obtained in which the values of *ko* and *E* were determined for different types of coal with different degrees of accuracy; there are also attempts to generalize these data.

The experimental values of the *ko* and *E* constants, in particular, the detailed characteristics given in the monograph of A. Predvoditelev et al., can be used for approximate technical calculations of coal (coke) burning. Therefore, the foregoing relations for heterogeneous combustion have not only a qualitative but also a quantitative value.

The amount of heat removed from a unit surface of coal per unit time, is written as:

$$Q_{II} = \alpha(T - T_o) \qquad (122)$$

where α [$kcal/m^3\ s\ deg$] is the coefficient of heat transfer by convection;

T and T_0 are, respectively, the temperature of the gases directly at the surface of the coal and far from it.

The first of these values (T), naturally, coincides with the temperature of the coal surface.

Equating expressions (121) and (122), we obtain the equation of the steady-state heat balance:

$$\alpha_D(c_0 - c)q = k_0 e^{-E/RT} cq = \alpha(T - T_0) \qquad (123)$$

We introduce, as before, the value of completeness of burning of the reacting gas:

$$\varphi = 1 - \bar{c} = 1 - \frac{c}{c_o} \qquad (124)$$

where $\bar{c} = \frac{c}{c_o}$ is the dimensionless concentration of the reacting gas.

Note that the value of φ in the heterogeneous process can be given the other physical interpretation. In the diffusion region of combustion, by definition, the concentration of the reagent gas at the surface of the coal is zero:

$$\bar{c} = 0 \qquad \varphi = 1 \qquad (125)$$

In this case, the amount of gas diffusing to the surface of the coal (that is, the quantity proportional to the rate of coal burnout from a unit surface) will obviously be equal to the product $\alpha_Д c_o$. Accordingly, the value

$$\varphi = 1 - \frac{c}{c_o} = \frac{\alpha_Д (c_o - c)}{\alpha_Д c_o} \qquad (126)$$

characterizes the degree of approximation of the process to the region of diffusion burning (the "diffusion measure").

Expression (126) can be written in the other form, convenient for practical calculations. Noting that its numerator $a_Д (c_0 — c)$ is the combustion rate per unit of the reaction surface, we introduce an additional equation for determining the amount of heat released per unit surface per unit time:

$$Q_1 = \alpha_D (c - c_0) q = kcq = k_{eff} \cdot c_0 q$$

where

$$k_{eff} = \frac{1}{\frac{1}{\alpha_D} + \frac{1}{k}} = \frac{1}{\frac{1}{\alpha_D} + \frac{e^{ER/T}}{k_0}} \qquad (127)$$

is a reduced (effective) reaction rate constant of the first one. It follows from (126) that

$$\varphi = \frac{k_{eff}}{\alpha_D}$$

i.e. the coefficient of completeness of combustion is equal to the ratio of the reaction rate k_{eff} to the gas-transfer coefficient α_d. In terms of physical meaning, this method of calculation is analogous to the addition of "resistances" in a series connection; the value $\frac{1}{\alpha_D}$ corresponds to the diffusion resistance, $\frac{1}{k}$ kinetic resistance, the total resistance is $\frac{1}{k_{эфф}} = \frac{1}{\alpha_{Д}} + \frac{1}{k}$. From the first equality in the system of equations (123), which expresses in two forms the same amount of heat released during the reaction, we find:

$$\varphi_1 = \frac{1}{1 + \frac{c^{1/\theta}}{k_o / \alpha_{Д}}} \qquad (128)$$

The dimensionless ratio of the quantities characterizing the reaction rate and the diffusion rate $\frac{k_0}{\alpha_D}$ can be replaced by the inverse ratio of the time characteristic for these processes, that is,

$$\tau_{DK} = \frac{\tau_D}{\tau_K} = \frac{k_0}{\alpha_D} \tag{129}$$

where $\tau_{Д}$ and $\tau_{К}$ are, respectively, the quantities characterizing the gas diffusion time to the reaction surface and the time of the last chemical reaction. Thus, formula (128) rewritten as (129)

$$\varphi_1 = \frac{1}{1 + \frac{e^{1/\theta}}{\tau_{DK}}} = \frac{\tau_{DK}}{\tau_{DK} + e^{1/\theta}} \tag{130}$$

coincides with the expression for $\varphi_1(\theta)$ in the previous chapter when the dimensionless time $\tau_{ПК}$ is replaced by the dimensionless time $\tau_{ДК}$ (that is, when the residence time is replaced by the diffusion time □Δ).

Let us consider the equality of the first and third expressions in the system of equations (123), that is, derivation of the expression $\varphi_{11}(\theta)$) for heat removal. From (123), taking (124) into account, we get:

$$\varphi_{11} = \frac{\alpha}{\alpha_D \cdot qc_0}(T - T_0) = \frac{E\alpha}{Rqc_0\alpha_D}(\theta - \theta_0) \tag{131}$$

Thus, here again the expression $\varphi_{11}(\theta)$ corresponds to a straight line in the diagram φ-θ, which is quite natural in connection with the adopted law of convective heat transfer (i.e., the adiabatic regime for the reacting gas).

Let us consider in more detail the ratio of the coefficients $\frac{\alpha}{\alpha_D}$ on the right-hand side of Eq. (131).

For the heat transfer coefficient α we will write an ordinary empirical equation in heat transfer for the connection between the criteria of similarity for forced convection:

$$\frac{\alpha d}{\lambda} = C\left(\frac{\omega d}{\nu}\right)^n \left(\frac{\nu}{a}\right)^m \tag{132}$$

where d is a characteristic size;

λ, ν and a are respectively the coefficients of heat conductivity, kinematic viscosity and thermal diffusivity of the gas;

ω is the relative velocity of the gas flow.

Similarly, for the gas recovery coefficient $a_{\text{д}}$, we can take:

$$\frac{\alpha_D d}{\rho D} = C\left(\frac{\omega d}{\nu}\right)^n \left(\frac{\nu}{D}\right)^m \tag{132a}$$

where D is the diffusion coefficient.

As both phenomena – heat exchange and gas exchange during combustion – occur under the conditions of the same process, and the phenomena of stimulated heat transfer and forced diffusion are analogous, the values of the empirical constants c, n and m in formulas (132) and (132a) can be taken practically the same. Then we get:

$$\frac{\alpha}{\alpha_D} = \frac{\lambda}{D}\left(\frac{D}{a}\right)^m = c_p\left(\frac{a}{D}\right)^{1-m} \tag{133}$$

where c_p is the average heat capacity of 1 m^3 of gas. As is known from heat transfer, the value of the exponent m in formula (132) for forced convection is small (m = 0.3 - 0.4); Therefore, taking into account the equality for gases $a \approx D$, we can approximately write $\left(\frac{a}{D}\right)^{1-m} \approx 1.$

Thus, approximately

$$\frac{\alpha}{\alpha_D} \approx C; \tag{134}$$

And it enables us to rewrite expression for $\varphi_{11}(\theta)$ in (131) as: $\varphi_{11} = \frac{1}{\upsilon}(\theta - \theta_o)$ (135)

where $\upsilon = \frac{Rqc_o}{Ec_p}$ is the characteristic of the calorific value of the reaction (or, for example, the oxygen content in the reacting gas).

As in the case of adiabatic combustion of a homogeneous mixture, expression (135) can be rewritten in the form

$$\varphi_o = \frac{\theta - \theta_o}{\theta_M - \theta_o}; \quad \theta_M = \theta_o + \upsilon \tag{135a}$$

It is important that here the similarity of the fields of temperature and concentration [formula (135a)] is a consequence of not only the adiabatic character of the process, but also the equality of the transfer coefficients: $a = D$.

Let us summarize our results. Both expressions for the curves in the diagram φ-θ, namely the heat release curve $\varphi_1(\theta)$-formula (130) and the heat-removal curve $\varphi_{11}(\theta)$ -formula (135), coincide with the analogous expressions used in the previous chapter.

The difference between formulas (130) for a heterogeneous process and for burning of a homogeneous mixture is that the first of them includes the quantity $\tau_{д}$, the characteristic time of diffusion, and the second $\tau_{П}$ - the residence time of the mixture in the chamber, in both cases in form of the relation to the characteristic time of the reaction τ_{K}.

It will be further shown that this difference leads to different physical interpretations of the critical phenomena of ignition and extinction, depending on the dimensionless time.

To find stationary regimes, as in the previous problem, we must use the equality

$$\varphi_1(\theta)=\varphi_{11}(\theta), \qquad (136)$$

and to determine critical conditions for ignition damping, we use the system of equations:

$$\varphi_1(\theta)=\varphi_{11}(\theta), \qquad \frac{d\varphi_1}{d\theta}=\frac{d\varphi_{11}}{d\theta} \qquad (137)$$

5.2 Thermal conditions of coal combustion

Let us apply the main results of the study of the heat regime of adiabatic combustion of a homogeneous mixture to the problem of coal combustion. As was shown in the previous chapters, the graphical solution of the heat balance equations in accordance with different conditions of intersection of the curves $\varphi_1(\theta)$ and the diagram $\varphi_{11}(\theta)$ lead to the possibility of existence of two types of the process – hysteresis and crisis-free. For the first of these three stationary reaction states are typical, two of which - the lower and upper ones - are stable, and the third - the medium - is unstable and practically not realized. The lower stationary regime corresponds to a weak heating of the coal surface and a very slow reaction; this is a slow oxidation regime. The upper stationary regime is characterized by high degree of the burning out of the reagent gas, the concentration of which at the coal surface is very small, and rapid burning out of coal; this is the combustion regime.

The surface temperature of the coal during combustion (upper mode) is close to the maximum:

$$\mathrm{T}_{max} = T_0 + \frac{qc_0}{c_p};$$

$$\theta_M = \theta_o - \upsilon$$

The fact that at the lower level there is practically no difference in the concentration of the reacting gas (its value at the surface is close to the value at a distance) allows us to identify this regime with kinetic combustion. Intensive diffusion is absent, and the process as a whole is determined by the temperature and kinetic characteristics of the fuel.

In contrast, the upper combustion regime is close to diffusion combustion (gas concentration at the surface) or in the region of small values of the parameter $\tau_{ДК}$ to the intermediate one.

Test questions:

1 What simplifications have been made in the theory of coal combustion?

2 Describe the general elementary concepts of the diffusion theory of combustion of a coal particle.

3 What is the amount of heat removed from a unit of coal surface per unit time?

4 Write down the equation of the steady heat balance

5 What is the temperature of the coal surface during burning?

REFERENCES

1 Khitrin L.N. Physics of combustion and explosion. - Moscow: Publishing house of Moscow University. - 1957 - 452 p.

2 Frank-Kamenetsky D.A. Diffusion and heat transfer in chemical kinetics. - Moscow: Nauka, 1987. - 502 p.

3 Zeldovich Ya.B., Barenblatt G.I., Librovich V.B., Makhviladze G.M. Mathematical theory of combustion and explosion. - Moscow: Nauka, 1980. - 478 p.

4 Spalding D.B. Fundamentals of the theory of combustion. Trans. from English. L.A. Klyachko, M.P. Samozvantseva, ed. D.N. Vyrubova. Moscow: Gos. Energy Publishing House, 1959. - 320 p.

5 Vulis L.A., Ershin Sh.A., Yarin L.P. Fundamentals of the theory of gas flare. L .: Energy. - 1968. - 204 p.

6 Fundamentals of the practical theory of combustion: a textbook for universities / V.V. Pomerantsev, K.M. Arefyev, D.B. Akhmetov et al.; Ed. V.V. Pomerantsev. 2 nd ed. - L .: Energoatomizdat., 1986. - 312 p.

7 Vulis, LA, Yarin, L.P. Aerodynamics of the torch. - L .: Energia, 1978. - 320s.

8 Spalding, D.B. Combustion and mass transfer. - M .: Machine-building, 1985. - 240 p.

9 Аскарова А.С., Болегенова С.А., Локтионова И.В., Шортанбаева Ж.К. Жазық каналда жану бар кездегі турбулентті жылумассатасымал// Известия Национальной Академии Наук РК, 2005.- № 2(240). – с. 31-38.

10 Askarova A.S., Loktionova I.V., Lavrischeva E.I. Numerical study of combustion of solid fuel before and after plasma treatment // Publishing House "Tyazheloye Machinostroeniye", Moscow, No. 11, 2006, p.10-13.

11 A.S. Askarova, S.A. Bolegenova, I.V. Loktionov Generalization of surface friction coefficients for combustion of me-

thane in a flat channel // Proceedings of the 4th Russian National Heat Exchange Conference, October 23-27, 2006, Moscow, 3, p. 183-186

12 A.S.Askarova, M.A. Gorokhovski, I.V. Loktionova, M.Zh. Ryspayeva. Influence of camera configuration on spraying and burning of liquid fuel // Izvestiya NAS RK, Physics and Mathematics Series, 2006. – No. 3 - C. 6 – 10

13 A.S. Askarova, M.A. Gorokhovski, I.V. Loktionov, M.Zh. Ryspayeva. Combustion of liquid fuels in the combustion chamber // Izvestiya NAS RK, Physics and Mathematics Series, 2006. - No. 3. - P. 10 - 14

14 A.S. Askarova, S.A. Bolegeneva, I.E. Voloshin, M.Zh.Ryspaeva Numerical study of the burning process of liquid fuel injected into the combustion chamber // Materials of the III International Scientific and Practical Conference "Actual problems of Energy ", Ekaterinburg, Russia, 2007. – p..174 - 177.

15 A.S. Askarova, S.A Bolegenova, I.V. Voloshin, M.Zh.Ryspaeva Influence of initial concentration of fuel on combustion of laminar and turbulent jets // Bulletin of KazNU, series physics, ^{1}3 (27) 2008. - Pp. 177-180.

16 A.S. Askarova, S.A.Bolegenova, M.Zh. Ryspayeva, I.E.Voloshina Application of the statistical model at the simulation of liquid fuel combustion // Izvestiya NAS RK, series phyz-math. No. 5 (261), 2008. - p. 51 - 54.

17 A.S. Askarova, S.A. Bolegenova, I.V. Voloshina, M.Zh.Ryspaeva Influence of the mass of injection of liquid fuel on its self-ignition and combustion // Izvestiya NAS RK, series fiz.mat., No. 2, 2009 - p.3-11.

18 A.S.Askarova, S.A.Bolegenova M.Zh.Ryspayeva, I.E.Voloshina Numerical study of dodecane’s combustion in the burner chamber// Bulletin of KazNU, series physics, No. 2(29), 2009. - p. 60 - 63

19 A.S.Askarova, M.A. Gorohovski, I.E.Voloshin, M.Zh.Ryspaeva Numerical modeling of combustion and self-ignition of two-phase chemically reacting flows with injections // Proceedings of Tomsk Polytechnic University. V.315. No.4. Power engineering. 2009. - p. 5-9.