

Lecture 8. Features of explosive reactions. N.N.Semenov theory of thermal explosion

The purpose of the lecture: to familiarize students with the features of explosive reactions, the N.N.Semenov theory of thermal explosion.

Expected results: students mastering knowledge about the features of explosive reactions, the essence and consequences of the N.N.Semenov theory of thermal explosion.

Burning seems to man as the main source of energy. With the advent of nuclear energy, the role of other energy sources has somewhat decreased, but it will be many more years before combustion loses its leading position.

Reflections on the nature of fire are undoubtedly as old as Stone Age myths. They played an important role in the development of many religions, as well as in the birth of chemistry as a science. Despite this, the combustion process has not yet been studied as well as, for example, nuclear processes and photosynthesis.

This lag can not be explained only by the lack of interest or unwillingness to make efforts, mainly due to the complexity of the combustion process. Even the simplest flame is a complex of simultaneously occurring reactions accompanied by heat and mass transfer phenomena.

Burning is the oldest technology of mankind, used for more than 1 million years. Currently, more than 90% of the energy is produced in the combustion process, therefore, its study is really relevant.

Combustion studies in the past have focused on the study of hydrodynamics, which includes total heat release by a chemical reaction.

Recently, each of these processes has received more detailed development, and the technique of measuring and studying the flame has reached such a level that many combustion problems can be solved.

There are chemical reactions that slowly develop over time and chemical reactions that occur explosively and are accompanied by unexpected manifestations - flashes, sound effects, etc.

The concentration decreases by chemical reaction and the reaction rate decreases. At higher temperatures, the reaction rate increases. The increase in the reaction rate at an elevated temperature occurs gradually and smoothly (for every 10 °C the speed doubles).

Such patterns are inherent in the non-explosive reaction $H_2 + J_2$.

Significant features of the explosive reaction were noted as early as the middle of the last century by Bunsen and Van Hoff. Depending on the temperature, the reaction rate changes very sharply.

So, for example, H_2+O_2 at room temperature and atmospheric pressure practically do not react for many years. With increasing temperature, the reaction rate remains immeasurably low up to a certain critical value, which depends on the experiment. For example, for a stoichiometric mixture of $2H_2 + O_2$ at atmospheric pressure – 550 °C. At a temperature slightly higher than T_{cr} , the reaction is very fast, the pressure rises rapidly and a vessel explosion can occur. The speed is so great that researchers of the last century could not study its kinetics in detail.

The main sign of an explosive reaction is the presence of a temperature at which the rate of a chemical reaction - the ignition temperature - changes abruptly. The same sharp change in the reaction rate can be obtained by changing the pressure at a given temperature.

When observing the explosive reaction, the first impression is that at T and P below the critical, there is nothing in the mixture or almost nothing happens, but when critical parameters are reached, everything immediately reacts. This feature of the process gave reason to call the reaction explosive (Fig. 8.1).

These are the data of Kowalski (1933), who was the first to experimentally demonstrate the possibility of chain ignition in isothermal conditions. ΔP - a value equal to the decrease in the total pressure in the system.

Thus, two characteristic features of the explosive reaction are the presence of the τ_{ind} induction period and the existence of critical conditions.

We proceed to consider the physical causes that cause the characteristics of explosive reactions. Very often, the explosive course of reactions is explained by the chain nature, the dependence of the reaction rate on the concentration of active centers formed during the reaction, and we will stop on them (H_2+O_2). So, chain reactions go through the formation of active particles.

Firstly, during the reaction, active particles can be formed as a result of thermal motion independently of the chain reaction, since the molecules of the starting material can dissociate upon impact; the speed of this process is low.

Secondly, there may be branching of the chain with an increase in free valency. The rate of formation of radicals is proportional to the concentration of radicals.

There is also the process of death - a collision with a stable molecule or as a result of diffusion to the walls, this speed is proportional to the concentration of radicals.

The expression for measuring the concentration of active centers in time has the following form

$$dn/dt = W^0 + fn - gn$$

denote $f - g = \varphi$, then

$$dn/dt = W_0 + \varphi n$$

where W_0 is the nucleation rate, f is the branching rate constant, g is the chain termination constant.

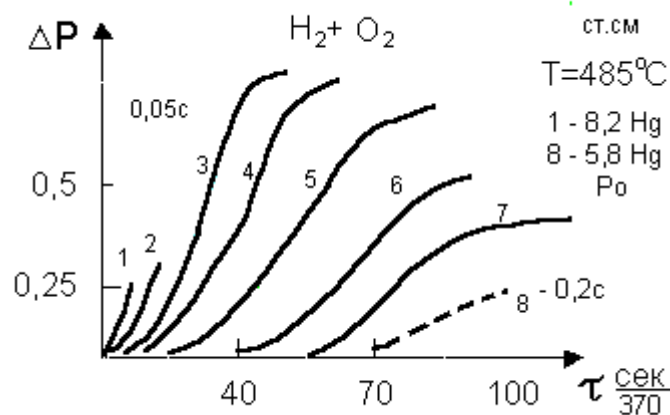


Fig. 8.1. Kinetic curves of combustion of a stoichiometric mixture of hydrogen with oxygen at 485 °C

A change in external conditions (T, P) causes a change in both f and g , and f - is more dependent on T than g , because E_{act} is not necessary for the death of active centers (such reactions proceed without breaking the connection). The difference $f - g = \varphi$ changes sign with increasing temperature; at low temperatures it is negative, at high it is positive. From consideration under natural initial conditions $t = 0, n = 0$ it follows that for $\varphi < 0$, i.e. at low temperatures, the concentration of active centers tends to the limit $W_0/(-\varphi)$, remaining small, with $dn/dt \rightarrow 0$.

For $\varphi > 0$, on the contrary, the rate of formation and concentration of active centers continuously increase. Thus, depending on the sign of φ , the type of solution changes dramatically. The temperature at which φ vanishes and will be just that T_{cr} below which explosion is impossible.

These qualitative considerations explain the existence of the ignition region of the explosive mixture at a fixed initial pressure and the transition of T_{ach} through the critical value, which corresponds to $\varphi = 0$.

Let us consider in more detail the properties of kinetic curves for various φ . To do this, we find the integral of the equation satisfying the conditions $n = 0$ at $t = 0$:

$$n = W_0/\varphi(e^{\varphi t} - 1)$$

Reaction rate i.e. the rate of formation of the final products is equal

$$W = \nu f n = \frac{\nu f W_0}{\varphi} (e^{\varphi t} - 1)$$

where ν is an integer of the order of unity, indicating how many molecules of the final product are formed as a result of the reaction of one active center

N.N.Semenov theory of thermal explosion

Let us consider the course of an exothermic chemical reaction in a closed vessel with a wall temperature T_0 . The gas temperature at the initial time is also equal to T_0 . The rate of heat in the vessel is

$$q_+ = QW$$

where W is the rate of a chemical reaction, Q is the heat of reaction.

The rate of heat transfer to the walls of the vessel is

$$q_- = \alpha S/V (T - T_0)$$

here α is the heat transfer coefficient, S/V is the area and volume of the vessel. The kinetics of the process is described by the equation

$$dT/dt = 1/(\rho C) (q_+ - q_-)$$

C –heat capacity at constant volume.

The conditions for the stationary course of reactions is the equality of the heat input and heat removal $q_+ = q_-$, which determines the possible values of the stationary values of the temperature in the vessel.

Let us consider the dependence of q_+ and q_- on temperature T under various heat transfer conditions (Fig. 8.2) q_+ increases with T as well as the reaction rate according to the Arrhenius law (curve 1), and the heat transfer rate q_- is linear (line 2).

Let the heat transfer be so significant that the straight line q_- intersects the heat transfer curve. Since $T_{\text{mix}} = T_0$ (vessel walls), there is no heat removal, heat is generated in the reaction - the temperature of the mixture begins to increase, the difference $T - T_0$ between the gas and the vessel wall grows, which leads to an increase in the heat removal rate.

At a certain gas temperature $T = T_F$ at the point F q_+ and q_- become equal, the gas will not be further heated.

If the gas is heated to $T^* \geq T_F$, the temperature drops to T_F , which indicates the stability of the stationary regime, which corresponds to point F , i.e. with significant heat transfer and the intersection of q_+ and q_- , the gas is heated to T_F close to T_0 and will continue to react for a long time at this temperature.

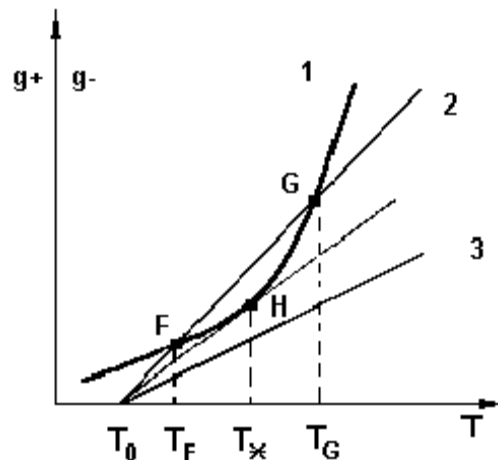


Fig. 8.2. The dependence of q_+ and q_- on temperature T under various conditions of heat transfer

The second point G - the intersection point, is carried out at $T = T_G$ corresponds to the unstable mode. Indeed, if T is slightly lower than T_G , then the speed q_+ will exceed the speed q_- and T will fall to T_F . If the gas is heated to $T > T_G$ then q_+ will be grow further. Thus, point G plays the role of a kind of watershed.

Let us analyze the system under the assumption that at the same temperature T_0 the heat transfer conditions have worsened (for example, a decrease in the S/V ratio).

The heat-release curve does not change, but the angular coefficient of the straight line q_- decreases and curve 1 will lie above this straight line at all temperatures - straight line 3. In this case, the reaction mixture begins to grow unlimitedly. Self-ignition will occur. There will be no stationary regime of an exothermic reaction.

You can come to the same result by changing not the heat transfer conditions, but the temperature of the walls T_0 . In this case, the slope of the direct heat sink will remain the same, but will shift in parallel in the direction of temperature change. Obviously, at $T_{01} < T_{01}$ there will be a stationary mode corresponding to the temperature T_F , at $T_{02} > T_{01}$ the lines do not intersect - an explosion occurs.

The highest wall temperature at which a stationary mode is possible is obviously T_{01} - in this case, the q_+ curve touches q_- .

From these arguments it is clear that the ignition ability of a mixture is not characterized by any physical constant related to the reactivity of the mixture, as the first researchers of the ignition phenomenon claimed.

In fact, self-ignition depends on the shape and size of the vessel, the thermal conductivity of the gas, etc., i.e. not only on the speed of a chemical reaction. V is const, S/V is different.

The principal circumstance of Semenov's theory is that the analysis of a seemingly purely unsteady process, such as an explosion (self-ignition), uses a stationary approach. The condition for the appearance of an unsteady regime - an explosion - is formulated as a condition for the disappearance of a stationary regime, i.e. the impossibility of a slow reaction with heat release balanced by a heat sink.

Semenov showed that although ignition does not occur at T_{cr} , but at high temperatures, the wall temperature determines many important characteristics of the process: ignition condition, reaction time, etc.

If, say, at 580 °C there is no ignition, but at 600 °C, this does not mean that at 600 °C the reaction rate is so high that it can cause the observed external manifestations of the explosion. In fact, at 600 °C, conditions are realized under which the reaction rate increases sharply, a high temperature is reached (1000-2000 K) at which the reaction rate is so high that it can cause a glow, a strong sound effect.

Literature

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