PHYSICAL CHEMISTRY

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1962

SovietRxiv

Abstract

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PHYSICAL CHEMISTRY

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COMBUSTION AT ELEVATED PRESSURES OF CONDENSED MIXTURES WITH A NONVOLATILE AND NONDECOMPOSING FUEL

(Presented by Academician V. N. Kondrat' ev on 26 III 1962)

Experiments were carried out to study the combustion of mixtures of $KClO_4$ with graphite and $KClO_4$ with tungsten. Both systems are characterized by the fact that only the oxidizer can decompose with formation of a gas phase (oxygen). Both types of "elemental" fuels (graphite, tungsten) have negligible vapor pressure at combustion temperatures. Smokeless powder, which is sometimes considered (1) as a model of a system with a nonvolatile fuel, is less characteristic in this respect.

The charcoal used in powder manufacture is capable of partial gasification; in addition, smokeless powder contains a volatile component—sulfur. The literature gives data (2) on the combustion of a mixture of ammonium perchlorate with a nonvolatile fuel—coke. However, ammonium perchlorate is capable of burning by itself, without fuel. In the mixtures we used, neither the fuel nor the oxidizer can burn separately. The combustion process is possible only through interaction of the fuel with the oxidizer, which, naturally, is represented either as a reaction of the liquid (molten) oxidizer with the surface of the fuel or as a reaction of gaseous oxygen, formed by decomposition of $KClO_4$, on the surface of the fuel particles—graphite or tungsten. It should be noted that in the case of graphite the initial formation of the lower gaseous oxide CO is possible, followed by reaction in the gas phase with formation of CO_2. For tungsten, an analogous possibility is difficult to imagine: the oxide WO_2 is nonvolatile.

Our experiments consisted mainly in determining the combustion rate (the rate of flame propagation) of compacted specimens at various pressures and various ratios of the components. The finely ground starting components (particle size of C, W, and $KClO_4$ on the order of several microns) were thoroughly mixed. The mixtures were pressed at a true pressing pressure of ~ 4500 atm in the form of cylinders 10 mm in diameter and 10–12 mm long. The prepared specimens were placed in a bomb of considerable volume, in which the required pressure was produced with compressed nitrogen. To measure the combustion rate, two methods were used: an optical method (recording the image of the moving flame on a moving film) and a method based on recording small pressure rises in the bomb (0.5-3 atm) during combustion of the specimens by sensitive piezoelectric

Fig. 1

Figure 1: Fig. 1

sensors mounted in the bomb. Processing of the curves $p(t)$ made it possible to correct the true pressure in the bomb, and also to determine the time interval between the beginning and end of combustion; the reliability of determining this interval was increased by special measures. We used mainly the latter method as the less laborious one. The specimens were ignited by a tungsten wire heated by an electric current. It should be noted that mixtures with graphite of stoichiometric composition (15% graphite and 85% $KClO_4$) and compositions close to it ignite with difficulty and burn unstably. In compositions with an excess of fuel, combustion is stable and begins more easily. Mixtures with tungsten ignite well and burn steadily both with an excess and with a deficiency of fuel.

We carried out experiments with a considerable number of different mixtures. Figure 1 presents selected data on burning rates at different pressures for four systems: 1) a mixture of 30 wt.% graphite and 70% potassium perchlorate ($\alpha = 0.4$); the graphite particles are relatively large (110–140 μ); 2) the same system: graphite particles of size 1-3 μ; 3) a mixture of 70% tungsten and 30% potassium perchlorate; $\alpha = 1.14$; 4) a mixture of 90% tungsten and 10% potassium perchlorate; $\alpha = 0.3$ ($\alpha = k/k_{\text{stoich}}$, where k is the weight ratio of oxidizer to fuel in the mixture and k_{stoich} is the corresponding stoichiometric ratio).

Fig. 1. Dependence of burning rate on pressure: **1, 2** –mixtures with graphite; **3, 4** –mixtures with tungsten. **1** –system 1 (see text), **2** –system 2, **3** –system 3, **4** –system 4. (Each division of the left ordinate axis corresponds to ten divisions of the right scale.)

For mixtures with graphite (curves 1 and 2), the scale of burning rates is plotted on the right. For very rapidly burning mixtures with tungsten (curves 3 and 4), the scale is plotted on the left. The measured burning rates of the mixtures vary over a wide range. The lowest established burning rate (with graphite) was 0.5 mm/sec; the highest (with tungsten) was 200 mm/sec.

Let us note some features of the combustion of the systems studied.

Dependence of the burning rate on pressure

Despite the substantial difference in burning rates, the dependence $u(p)$ for most mixtures proved similar and, in general, significant. For mixtures with graphite and for mixtures with tungsten not too far from stoichiometry, Vieille' s law is satisfied,

$$u = bp^n,$$

where the values of the constants b and n depend in a complicated way on the ratio between fuel and oxidizer, on the particle size of the fuel, etc.; in particular, the value of n varies within the range 0.3-0.7. For a system with a definite component ratio, the values of n over the entire range of pressures studied (5-100 atm) are practically constant. The substantial dependence of the burning rate on pressure (up to $u \sim p^{0.7}$) indicates that the reaction proceeds with some participation of the gas phase.

Dependence of the burning rate on the size of the fuel particles

The character of this dependence was investigated qualitatively in this work. As already noted, curves 1 and 2 correspond to mixtures with the same ratio of graphite to oxidizer, differing in the size of the fuel particles. In going from 1 to 2, the particle size decreases by a factor of 50-100, while the burning rate, as is seen from Fig. 1, increases by a factor of 10. Such a dependence is strong in comparison with systems in which both the fuel and the oxidizer, during combustion, form a gas or smoke-gas phase. In the latter, when the particle size is changed by a factor of 100, the burning rate changes only by a factor of 1.5-2.0 ([3]).

Influence of the ratio between oxidizer and fuel

For the systems studied, the dependence of the burning rate on the component ratio is quite distinctive. Some of the results obtained, relating to a pressure of $\sim$ 30 atm, are presented in Fig. 2. The value α of the mixtures was taken as the characteristic of the component ratio ($\alpha = 1$ –stoich-

metry; $\alpha < 1$ means an excess of fuel). Along the ordinate are plotted the relative burning rates of the given system $u_\alpha / u_{\alpha=1}$ (the ratio of the burning rate of the given mixture to the burning rate of the stoichiometric mixture).

Curve 1 gives the data for a mixture of dextrin with $KClO_4$. In this system both the fuel and the oxidizer decompose, forming a gaseous or smoke-gas phase, in which the reaction determining the burning rate takes place. The maximum burning rate is reached at $\alpha < 1$, but in the immediate vicinity of $\alpha = 1$. With a substantial decrease in the value of α, the burning rate of such a mixture begins to fall, down to extinction of combustion. Curve 2 gives the data for mixtures with graphite (for small particle size), and curve 3 for mixtures with tungsten. Curves 2 and 3—for systems with "surface combustion" —differ substantially from curve 1, the system in which, during combustion, mixing of the gasifying fuel and oxidizer occurs. As the excess of fuel is increased, the burning rate of the graphite—potassium perchlorate and tungsten—potassium perchlorate systems increases, and at very large excesses of fuel ($\alpha = 0.1$-0.2) it is several times greater than in stoichiometric compositions. Mixtures with tungsten burn steadily up to a tungsten content of $\sim$ 97%. A mixture of 95% W—5% $KClO_4$ ($\alpha = 0.14$; combustion temperature $\sim 2000^\circ$ K) burns at a very high rate of 200

Figure 2

Figure 2: Figure 2

mm/sec; moreover, this rate depends only very weakly on pressure. It must be emphasized that the dependence $u(\alpha)$ changes when the particle size changes. Curve 2 with a maximum (Fig. 2) was obtained for a mixture with fine graphite. If coarse graphite is used, the dependence will be closer to curve 3, obtained for a mixture with tungsten. In connection with the results obtained, let us note the following: the laws of combustion of systems with a nonvolatile fuel have been the subject of theoretical studies ([1,4]). Conclusions were drawn for two limiting cases: kinetic and diffusion-controlled reaction regimes.

Fig. 2. Dependence of $u_\alpha/u_{\alpha=1}$ on α for a gasifying system and a system with "surface" combustion (explanation in the text)

Theoretical conclusions for the kinetic regime give too strong a dependence $u(p) \to u \sim p$. Theoretical conclusions for the diffusion regime give too strong a dependence on particle size, $u \sim l^{-1}$. It is also very important to emphasize the following: in the indicated theoretical studies the question of the role of the component ratio was in fact bypassed; the conclusions of all these works refer mainly to one case, when there is very little fuel. In reality, such mixtures burn very poorly, or practically do not burn at all, as, for example, mixtures with graphite. Meanwhile, our data show that when the weight ratio is changed, i.e., when the value of α of the mixtures is changed, the character of the dependences and, in particular, the character of the dependence $u(p)$ changes radically.

Approximately our results may be explained by the following scheme. As already noted above, it is natural to assume that the reaction proceeds on the surface of the fuel particles and that the rate of the chemical reaction W is proportional to the specific surface S (surface per unit volume). As the particles are ground finer and their size decreases, the specific surface increases: $S \sim 1/l$, where l is the mean particle size. If $W \sim l^{-1}$, then, since the burning rate $u \sim W^{0.5}$ (a conclusion following, in particular, from the combustion theory of Zel' dovich and Frank-Kamenetskii), then $u \sim l^{-0.5}$. One may further assume that the dependence of the burning rate on pressure is associated either with an increase in the concentration of oxygen at the particle surface, or with

with an increase in the amount of oxygen adsorbed on the surface. Under these assumptions $W \sim p$ (in the case of adsorption the dependence may also be weaker); since $u \sim W^{0.5}$, we obtain $u \sim p^{0.5}$, or somewhat weaker.

These conclusions, in general, do not contradict the results we obtained. As for the very high burning rate of mixtures with a large excess of tungsten, it should be noted that the thermal conductivity of such mixtures must be considerable and must increase as the tungsten content increases. In the combustion of gasifying components, the thermal conductivity of the gaseous (smoke-gas) phase is important. Changes in the latter are usually small and are masked by other factors. If the burning rate is determined by the reaction in the condensed phase, then, since the thermal conductivity λ can change substantially, the burning rate will also change, $u \sim \lambda^{0.5}$. In addition, for the systems considered, dilution with fuel increases the specific surface area, especially relative to the weight of the oxidizer.

P. F. Pokhil showed[5] that combustion of gasifying systems, as a rule, must be accompanied by dispersion—the formation of very fine particles of smoke size. The facts set forth above indicate that the reaction on the surface of particles can proceed at a high rate and provide a high burning rate.

Since, during dispersion, the specific surface area is very large, one must also take into account the possibility of an effective reaction of intermediate gaseous products on the surface of particles formed in the process of dispersion of the condensed phase.

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Received
23 III 1962

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