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Abstract

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ON THE DEPENDENCE OF THE TEMPERATURE COEFFICIENT OF THE BURNING RATE OF EXPLOSIVES AND PROPELLANTS ON PRESSURE

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If a propellant or an explosive burns with a linear rate u_1, then, when the initial temperature is increased by ΔT, its burning rate will increase and become

$$u_2 = u_1 e^{\alpha \Delta T}. \tag{1}$$

For finite temperature differences the temperature coefficient of the burning rate is

$$\alpha = \frac{\ln(u_2/u_1)}{\Delta T} \frac{1}{\text{deg}}.$$

It has been established (^{1}) that α for smokeless nitroglycerin propellant decreases with increasing pressure at which combustion occurs. We compared this circumstance with the well-known fundamental fact that the heat and the combustion temperature of smokeless propellants increase, up to a certain limit, with increasing pressure.

In Fig. 1, curve 1 shows the variation of the temperature coefficient with pressure. The points were obtained by recalculating literature data (^{2}) for the temperature interval 0–25°. In the same figure, curve 2 gives the variation of the maximum flame temperature according to data (^{3}). Comparison of the two curves indicates their undoubted relationship. In the region of low pressures, α and T change appreciably (α decreases rapidly; T increases rapidly). At the same value $p = 50$ atm, α and T become constant. It should be noted that the data on α and T refer to propellants of different grades; however, the general character of the relationship is beyond doubt.

Fig. 1. Dependence of the temperature coefficient of the burning rate α (1) and the combustion temperature T of nitroglycerin propellant on pressure p

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We determined the temperature coefficient at various pressures for a model mixture of potassium perchlorate (87%) and bitumen (13%). The methods for preparing the charges were described in (^{4}). It was found that at atmospheric pressure $\alpha = 1.5 \cdot 10^{-3}$ deg^{-1}, while at $p = 22.5$ ata $\alpha = 1.4 \cdot 10^{-3}$ deg^{-1}, i.e., it changes hardly at all. The experiments were carried out while changing the initial temperature from -50 to $+80°$; the points lie well on the straight line $\lg u$—T_0. At our request, R. Kh. Kurbangalina established that the heat of combustion of this mixture also remains almost constant when the pressure is changed. Thus, the temperature coefficient decreases with increasing pressure if, in the given pressure interval, the combustion temperature (heat) increases, and remains constant if the temperature does not change.

The relation between α and T can be obtained from the theory of Ya. B. Zel' dovich (^{5}), according to which

$$u_1 = cT_r^n e^{-E/2RT_r}, \tag{2}$$

where E is the activation energy; T_r is the maximum combustion temperature; n is determined by the nature and order of the reaction; c is a coefficient including parameters that do not depend on T_r.

Let us neglect the power-law dependence in comparison with the exponential one; then

$$u_1 \simeq c' e^{-E/2RT_r}. \tag{3}$$

Increase the initial temperature of the system by ΔT. Then approximately

$$(T_r)_2 = T_r + \Delta T, \qquad \frac{u_2}{u_1} = \frac{\exp(-E/2R(T_r + \Delta T))}{\exp(-E/2RT_r)}.$$

Assuming that $\Delta T \ll T_r$, we obtain

$$u_2 \simeq u_1 e^{\frac{E}{2RT_r^2}\Delta T}. \tag{4}$$

Comparing (4) and (1), we have

$$\alpha \simeq \frac{E}{2RT_r^2}. \tag{5}$$

It should be noted that if we had not neglected the power-law dependence on T_r, then accordingly we would have obtained

$$\alpha \simeq \frac{E}{2RT_r^2} + \frac{n}{T_r},$$

where $n = 5/2$ for a bimolecular reaction; $n = 3/2$ for a monomolecular reaction in the gas phase.

It follows from (5) that α must decrease with increasing T_r; the higher T_r, the less the preliminary heating by ΔT should affect it.

Here a very substantial reservation must be made. Because of the complexity and multistage character of combustion reactions, the "leading" reaction, i.e., the reaction that provides the greatest volumetric rate of heat release and basically determines the combustion rate of the system, very often proceeds not at the maximum temperature T_r, but at a relatively low temperature, which we shall conventionally call the "effective" temperature (T_{eff}).

P. F. Pokhil (^{6}) showed that, during the combustion of smokeless powder, T_{eff} is considerably lower than T_r. P. F. Pokhil, V. M. Mal' tsev, and G. V. Lukashenya (^{7}), using an exact optical method, showed that for nitroglycerin powder $T_{\text{eff}} = 1300$–1400°K ($T_r = 2500$–2600°K). Still earlier, one of us (^{8}) showed that for nitroglycol (which evaporates and burns in the gas phase) $T_{\text{eff}} \simeq 1650$°K, whereas $T_r \simeq 3500$°K.

The indicated circumstances do not contradict the conclusions that were drawn from Zel'dovich's theory. It is only necessary: 1) to operate with the temperature T_{eff} instead of T_r; 2) to assume that $(T_{\text{eff}})_2 = (T_{\text{eff}})_1 + \Delta T$. Both of these propositions were used by one of us in a study of the combustion of nitroglycol (^{8}).

Let us note, incidentally, that earlier (Fig. 1) we compared the change of α and T_r. It should be assumed that when the pressure changes (within a certain interval), T_{eff} changes in the same way as T_r; this is in general agreement with experimental data (^{7}). Taking the considerations set forth into account, we obtain

$$\alpha \simeq \frac{E}{2RT_{\text{eff}}^2}. \tag{6}$$

Expression (6) relates the quantities α, E, and T_{eff}. It is natural to try to use it for an approximate estimate of T_{eff}, since α is determined experimentally, while the value of E can be estimated by known methods. We have

$$T_{\text{eff}} \simeq \sqrt{\frac{E}{2R\alpha}}. \tag{6a}$$

Here it is only necessary to emphasize that if the Arrhenius law underlying (6a) is universal for all types of combustion (provided that the combustion rate is determined by kinetics), then the condition $(T_{\text{eff}})_2 \simeq (T_{\text{eff}})_1 + \Delta T$ is apparently not always satisfied. Let us apply relation (6a) to substances with known α and E.

1. **Nitroglycol** ([8]). $E = 37\,000$ cal/mole; $\alpha = 4.5 \cdot 10^{-3}$ deg^{-1}. Then $T_{\text{eff}} \simeq 1400°$ K. Previously the ideal T_{eff} had been estimated as 1650° K. The agreement is sufficiently good (with a correction for the power-law dependence on temperature, the agreement would be better).
2. **Mercury fulminate** ([9,1]). $E = 25\,000$ cal/mole; $\alpha = 5 \cdot 10^{-3}$ deg^{-1}. Then $T_{\text{eff}} \simeq 1100°$ K. It has been noted that the temperature of the "leading" reaction during combustion of mercury fulminate is much lower than the flame temperature ($\sim 3600°$ K).
3. **Tetryl** ([1]). $E \simeq 50\,000$ cal/mole; $\alpha = 2.5 \cdot 10^{-3}$ (in the interval 100–200°). Then $T_{\text{eff}} \simeq 2200°$ K. This temperature is close to the maximum flame temperature. In this case, as also in others where α is relatively small ($\alpha = 1.5$–$2.5 \cdot 10^{-3}$ deg^{-1}), apparently the simplest original version of Ya. B. Zel' dovich' s theory is realized (the leading reaction proceeds at a temperature close to T_1). From this point of view, it is precisely small values of α that should be considered "normal." Increased values of α mean that the "leading" reaction proceeds in a zone of comparatively low temperatures.

Let us apply expression (6a) to the more complex case of combustion of nitroglycerine powder. We take $E = 40\,000$ cal/mole. According to ([2,10]), at elevated pressures $\alpha \simeq 4 \cdot 10^{-3}$ deg^{-1}.

According to A. D. Margolin and O. I. Nefedova ([11]), at a pressure of 50 atm, $\alpha \simeq 5 \cdot 10^{-3}$ deg^{-1}. Taking this value, we obtain $T_{\text{eff}} \simeq 1400°$ K, which is very close to the value determined experimentally ([7]). It was shown ([12]) that at atmospheric pressure, with increasing temperature, α of nitroglycerine powder sharply increases (from $\sim 2 \cdot 10^{-3}$ at $T_0 < 18°$ to $\sim 14 \cdot 10^{-3}$ at $T_0 > 40°$).

On the basis of the general propositions of Ya. B. Zel' dovich' s theory, A. D. Margolin ([13]) came to the interesting conclusion that at elevated temperatures the reaction in the condensed phase of the powder becomes the "leading" one.

Let us apply relation (6a) to this case. $E = 40\,000$ cal/mole, $\alpha = 14 \cdot 10^{-3}$ deg^{-1}. Then $T_{\text{eff}} \simeq 850°$ K. The maximum temperature of the condensed phase of the powder ([6]) is $\sim 600°$ K. In order to obtain from (6a) $T_{\text{eff}} = 600°$ K, it is sufficient to assume either that in reality $E = 25\,000$ cal/mole (which A. D. Margolin in fact did), or that in this case the condition $(T_{\text{eff}})_2 = (T_{\text{eff}})_1 + \Delta T$ is not satisfied.

Indeed, the maximum temperature on the surface of the condensed phase may vary according to a complex law in accordance with the kinetic dispersion. If, for example, we assume $(T_{\text{eff}})_2 = (T_{\text{eff}})_1 + \Delta T/2$, then for T_{eff} we obtain a value of approximately 600° K (with the value $E = 40\,000$ cal/mole). Finally, one may assume that in the case under consideration the combustion rate depends both on the reaction in the condensed phase ($T \simeq 600°$ K) and on the reaction in the smoky-gas phase ($T \simeq 1300$–$1400°$ K); as a result, applying (6a), we obtain a certain intermediate value $T_{\text{eff}} \simeq 850°$ K.

At the same time, it is necessary to emphasize the validity of A. D. Margolin' s proposition: with an increase in the initial temperature, the role of low-temperature reactions in the condensed phase must indeed in—

increase. From the work of A. D. Margolin (^{13}), however, one may conclude that, with increasing pressure, the role of the condensed phase should become increasingly dominant. The "moderate" values of α observed at high pressures cast doubt on this conclusion.

Let us note that at atmospheric pressure, for $T_0 < 18°$, $\alpha \simeq 2 \cdot 10^{-3}$ deg^{-1}. Hence, according to (6a), $T_{\text{eff}} \simeq 2200°$ K, which is very close to T_g. A somewhat unexpected conclusion is obtained: for $T_0 < 18°$ and $p = 1$ ata, the "leading" reaction in the combustion of nitroglycerin powder is the reaction in the high-temperature region. This, of course, does not imply that the reaction in the smoke-gas phase is to be "eliminated." One may suppose, for example, that this most important stage of combustion is shifted into the region of high temperatures.

Because of the great complexity of the reactions in the combustion of nitroglycerin powder, the application of (6a) gives less definite results than in case c. Here, however, it should be emphasized that relation (6a) leads to a number of interesting nontrivial conclusions. Verification of these conclusions is a task for further experimental investigations. One of the primary tasks, in particular, should be to verify the somewhat paradoxical conclusion that at low temperatures and atmospheric pressure the burning rate of the powder is determined by reactions in the high-temperature zone. If this conclusion is not confirmed, it will be necessary to indicate why, under these conditions, α is so small.

Relation (6a) cannot be applied directly to the combustion of complex mixed systems, in particular those including solid particles (which do not evaporate and do not gasify). For example, (6a) cannot be applied directly to the combustion of black powder.

Nevertheless, in some cases (6a) can be applied also to mixed systems. Thus, for the model mixture of potassium perchlorate and bitumen mentioned above, if the particles of $KClO_4$ are sufficiently finely ground, the reaction proceeds in the kinetic regime (^{4}) (the components have time to mix before reaction). Let us take for the mixture $KClO_4$ with bitumen $E = 30\,000$ cal/mole; $\alpha = 1.4 \cdot 10^{-3}$ deg^{-1}. Then, from (6a), $T_{\text{eff}} \simeq 2300°$ K. Apparently, in this case the reaction proceeds at comparatively high temperatures, not far from the maximum ones.

From the foregoing one may conclude that a cautious, critical application of relation (6), which gives a connection between α and T_{eff}, may prove to be a useful auxiliary tool in studying the combustion mechanism and in establishing the nature of those reactions which determine the burning rate.

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