Physical Chemistry

1964

SovietRxiv

Abstract

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Physical Chemistry

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Linear Pyrolysis of Condensed Substances

(Presented by Academician V. N. Kondrat' ev on 6 IV 1964)

Linear pyrolysis is understood to mean the stationary, one-dimensional propagation of the front of a thermal decomposition reaction under conditions in which the condensed substance, located at some distance from the reaction zone, does not have time to heat up to the temperature at which the reaction proceeds at an appreciable rate. The regularities of linear pyrolysis must be known in order to determine the temperature above which the results of experiments on the kinetics of thermal decomposition of a substance in a medium with constant temperature become incorrect.

In apparatus for studying linear pyrolysis ([1]), a sample of the substance is pressed with a constant force against a heated metal plate; the rate of displacement of the sample (equal to the rate of linear decomposition of the substance) and the temperature of the plate T_0 at the place of contact with the surface of the substance are recorded.

The question of the dependence of the rate of linear decomposition on the surface temperature, as well as of identifying the latter with the temperature of the heater plate, is widely discussed in the literature.

Cantrell ([2]) solved the problem of the viscous motion of gaseous decomposition products in the gap between the end face of a cylindrical sample and the plate and showed that, in the pyrolysis of solid carbon dioxide at comparatively low temperatures, the temperature drop across the thickness of the gap is considerable (more than 100°). On the basis of his experiments, Cantrell cast doubt on the results of works ([3–6]), whose authors, studying the pyrolysis of high-molecular compounds (polystyrene, polymethyl methacrylate, etc.), assumed the temperature of the surface of the substance to be equal to the temperature of the plate.

In all experimental works on linear pyrolysis known to us ([3–6, 11]), it is assumed that the rate of linear decomposition u is related to the activation energy of the thermal decomposition process E by the relation

$$u \sim e^{-E/RT_1}. \tag{1}$$

It can be shown that this dependence is valid under certain conditions ([6]) only

Figure 1

Figure 1: Figure 1

for the case of a transformation process taking place essentially on the surface in a monomolecular layer (sublimation, evaporation). In this case, instead of the quantity E, expression (1) must contain the latent heat of the phase transition. The values of E calculated by formula (1) ([3]) are considerably smaller than the values of the activation energy determined from experiments on decomposition under isothermal conditions.

The solution of the problem of the velocity of propagation of the reaction front for a zero-order reaction proceeding in a layer of finite thickness gives the following expression ([7]):

$$u = \sqrt{\frac{\lambda_t R T_1^2 k_0}{\gamma_t E \left[c_t (T_1 - T_\infty) + Q/2\right]} e^{-E/RT_1}}, \tag{2}$$

where λ_t, c_t, γ_t are, respectively, the thermal-conductivity coefficient, heat capacity, and density of the substance, T_1 is the temperature of the surface of the substance, T_∞ is the tempe-

temperature of the substance far from the reaction zone, k_0 is the preexponential factor, Q is the heat effect of the reaction, and R is the universal gas constant.

It follows from (2) that, to a first approximation, the activation energy calculated by formula (1) is half the true activation energy. Let us note that Zel' dovich was the first to draw attention to this circumstance ([8]).

The aim of the present work is to elucidate the character of the decomposition reaction during the pyrolysis of high-molecular compounds (using polymethyl methacrylate as an example), to compare the temperatures T_1 and T_0, and also to assess the possibilities of the linear pyrolysis method for determining the kinetic constants of high-temperature decomposition of condensed substances.

In our experiments on the linear pyrolysis of polymethyl methacrylate (PMM), the linear decomposition rate u (cm/sec), the temperature of the plate T_0, °K, and the heat flux to the surface of the specimen q_1 (W/cm^2·sec) were recorded. For analysis, experiments were selected in which these quantities remained essentially constant.

Fig. 1. Surface of a polymethyl methacrylate specimen at various rates of linear decomposition (70×):
a –$58 \cdot 10^{-3}$ cm/sec; b –$20 \cdot 10^{-3}$ cm/sec;
v –$3 \cdot 10^{-3}$ cm/sec

In the course of decomposition in a thin surface layer of the substance, the appearance of bubbles of the gas phase is clearly visible, indicating the volumetric

Figure 2

Figure 2: Figure 2

character of the decomposition reaction. With increasing pyrolysis rate, the distance from the surface at which gas bubbles begin to appear (the thickness of the reacting layer) decreases; accordingly, the diameter of the bubbles at the moment they emerge at the surface also decreases.

Figure 1 shows photographs of the surface of PMM specimens at different rates of linear decomposition.

The solution we obtained for the problem of viscous flow of a gas in the gap between a flat specimen and the plate gives the following expression for the gap thickness z_1 and the temperature of the surface of the substance T_1:

$$z_1 = b\left(\frac{l\mu u\gamma}{W\gamma_{\text{g}}}\right)^{1/3}, \tag{3}$$

$$T_1 = T_0 - \frac{q_1 z_1}{\lambda_{\text{g}}}, \tag{4}$$

where b and l are, respectively, the width and length of the specimen surface; μ, λ_{g}, and γ_{g} are the viscosity, thermal conductivity, and density of the gas; W is the force with which the specimen is pressed against the plate. The values of the thermophysical constants of the gas were taken for the heavy hydrocarbon octane ([9]) and were referred to the temperature of the plate. At the highest recorded pyrolysis rates, the calculated thickness of the gas gap did not exceed $30\,\mu$. Figure 2

Fig. 2. Change in the temperature drop across the gas film with increasing pyrolysis rate

shows the dependence of the temperature drop $\Delta T = T_0 - T_1$ across the gas film on the pyrolysis rate.

the dependence of the temperature drop ΔT across the film on the pyrolysis rate is presented. It is obvious that, over a wide range of pyrolysis rates, the value of ΔT is relatively small in comparison with T_0, °K.

In Fig. 3 the dependences of $\ln u$ on $1/T_0$ and $1/T_1$ are presented. As shown above, at comparatively low rates these curves merge. To determine the kinetic constants k_0 and E, we transform expression (2), eliminating from it the heat effect Q with the aid of the heat-balance equation:

$$q_1 = u\gamma_\tau\left[c_\tau(T_1 - T_\infty) + Q\right]. \tag{5}$$

The desired expression will have the following form:

Fig. 3 and Fig. 4

Figure 3: Fig. 3 and Fig. 4

$$J = \frac{u\left[u\gamma_\tau c_\tau (T_1 - T_\infty) + q_1\right]}{2\lambda_\tau T_1^2} = \frac{R\tilde{k}_0}{E} e^{-E/RT_1}. \tag{6}$$

The processing of the experimental data by formula (6) is shown in Fig. 4. The kinetic constants calculated from this graph are, respectively: $E = 25.3$ kcal/mole; $k_0 = 3.6 \cdot 10^7$ sec^{-1}.

Fig. 3. Dependence of the rate of linear pyrolysis on the temperature of the plate and the surface temperature.
1 $-\ln u = f(1/T_1)$,
2 $-\ln u = f(1/T_0)$.

Fig. 4. Determination of the kinetic constants of the linear decomposition of polymethyl methacrylate.

Although, under conditions of slow decomposition, PMM decomposes by 99% to monomer ([10]), in the regime of linear pyrolysis a considerable part of the substance does not have time to decompose completely—a large amount of products of incomplete decomposition is released in the form of smoke. The value of the heat effect Q estimated from (5) in all experiments was substantially less than the heat expended on heating the substance from the initial temperature T_∞ to T_1. As a result, and also because of the absence of data on the dependence of the heat capacity of PMM on temperature, it is not possible to calculate an exact value of Q during pyrolysis.

In the case $Q/2 \ll c_\tau(T_1 - T_\infty)$, formula (2) has the form:

$$u = \sqrt{\frac{RT_1^2}{E(T_1 - T_\infty)}\, ak_0 e^{-E/RT_1}}, \tag{7}$$

where a is the thermal diffusivity coefficient of the substance.

The values of E and k_0, calculated by formula (7), are close to the values determined above and are $E = 24$ kcal/mole, $k_0 = 1.7 \cdot 10^7$ sec^{-1}.

Thus, it may be asserted that in experiments on the linear pyrolysis of high-molecular substances (of the PMM type), the decomposition reaction proceeds in a layer of finite thickness and, to a first approximation, the activation energy of the observed process is half the true activation energy of the thermal decomposition reaction; the surface temperature of the substance is close to the temperature of the plate over a wide range of pyrolysis rates.

The authors are sincerely grateful to B. I. Brounshtein, O. M. Todes, I. I. Paleev, and also to A. F. Belyaev for their attention to the work.

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Received
1 IV 1964

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Note: Figure translations are in progress. See original paper for figures.