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Abstract

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Academician of the Academy of Sciences of the BSSR M. M. PAVLYUCHENKO and E. A. PRODAN

ON THE ROLE OF CHEMICAL AND CRYSTALLIZATION PROCESSES IN REVERSIBLE TOPOCHEMICAL REACTIONS

Heterogeneous chemical reactions proceeding with the participation of solids include, in addition to chemical processes, crystallization processes associated with the destruction of the crystal lattice of the initial substances and, in most cases, the formation of a new crystal lattice of the reaction products. In the latter case, nuclei of the new phase are formed and grow. The laws governing this process in the presence of the solid phase of the parent substance, from which a new solid phase is formed as a result of a chemical reaction, are unknown to us. The question of the role of the chemical and crystallization processes in the observed reaction rate, their interrelation, and the influence of each of them on the other and on the total process has likewise not been studied at all.

In the case of reversible reactions, as has been shown for the decomposition reactions of carbonates ([1–7]), crystal hydrates ([8–10]), etc., the character of the kinetic curves depends on the distance from equilibrium at which the reaction proceeds. In vacuum, decomposition begins at the maximum rate, which in the course of time decreases to zero; near equilibrium, a maximum appears on the rate-time curves, which is attributed to the difficulty of formation of nuclei of the new phase. Therefore, at distances not far from equilibrium, the rate of formation of the new phase may prove decisive in the total process of solid-phase reactions. The work of formation of stable nuclei from the gas phase or from solution is determined, as is known, by the equation

$$A = \frac{16\pi\sigma^3 M^2}{3R^2T^2\rho^2\left(\ln\frac{P}{P_0}\right)^2}. \tag{1}$$

It follows from this that at a supersaturation equal to unity the work is equal to infinity, and, consequently, stable nuclei of the new phase will not arise.

Clarification of the role of supersaturation, and therefore also of crystallization processes, in reactions is of considerable scientific interest. We shall consider some of these questions for reactions that proceed reversibly.

Let the reaction proceed

$$\mathrm{AB_t} \underset{K_2}{\overset{K_1}{\rightleftarrows}} \mathrm{A_t} + \mathrm{B_g} - Q.$$

Its rate is equal to

$$V = K_2 S\{f(P_{0\mathrm{g}}) - f(P_\mathrm{g})\}, \tag{2}$$

where $P_{0\mathrm{g}}$ is the equilibrium pressure; P_g is the specified pressure; $f(P_{0\mathrm{g}})$ and $f(P_\mathrm{g})$ are the corresponding amounts of adsorbed gas.

As a first approximation one may set

$$f(P_{0\mathrm{g}}) = aP_{0\mathrm{g}}^n; \qquad f(P_\mathrm{g}) = aP_\mathrm{g}^n; \qquad n \ll 1. \tag{3}$$

For a relatively small temperature interval one may take

$$P_{0r} = Ce^{-Q/RT}. \tag{4}$$

The reaction rate

$$V = KS, \qquad K = K_2 a\,[C^n e^{-nQ/RT} - P_r^n]. \tag{2a}$$

Substituting, in place of K, its value $K^0 e^{-q_1/RT}$, in place of K_2 the quantity $K_2^0 e^{-q_2/RT}$, and assuming that $a = a_0 e^{\lambda/RT}$ and that n does not depend on temperature, we obtain, for $P_r^n = 0$,

$$q_1 = q_2 + nQ - \lambda. \tag{5}$$

For $n = 1$ we obtain the equation $q_1 = q_2 + Q - \lambda$; in all other cases

$$q_1 < q_2 + Q - \lambda. \tag{6}$$

Let us consider two more cases.

Case 1. The reaction proceeds at constant supersaturation or undersaturation and at different temperatures. In this case

$$K = K_2 a \left[\left(\frac{P_{0r}}{P_r}\right)^n - 1\right] P_r^n. \tag{7}$$

If the supersaturation at different temperatures remains constant, then

$$\left(\frac{P_{0r}}{P_r}\right)^n = \text{const}. \tag{8}$$

Substituting expression (8) into equation (7), and substituting their values for K, K_2, and P_{0r}^n, we obtain

$$K^0 e^{-q_1/RT} = K_2^0 e^{-q_2/RT} a\,[\text{const} - 1]\,\frac{C^n e^{-nQ/RT}}{\text{const}}, \tag{9}$$

whence

$$q_1 = q_2 + nQ - \lambda.$$

Thus, the activation energy found from the reaction rate at different temperatures and identical supersaturations is a constant quantity, not changing at other values of the supersaturation, and is equal to the activation energy of decomposition in vacuum (equation (5)).

Case 2. The reaction proceeds at different temperatures and the same gas pressure. In this case

$$\frac{q_1}{RT^2} = \frac{q_2}{RT^2} + \frac{d}{dT}\ln(C^n e^{-nQ/RT} - P_r^n) - \frac{\lambda}{RT^2} =$$

$$= \frac{q_2}{RT^2} + \frac{nQ}{RT^2}\,\frac{C^n e^{-nQ/RT}}{(C^n e^{-nQ/RT} - P_r^n)} - \frac{\lambda}{RT^2}. \tag{10}$$

It follows from equation (10) that when $P_r^n = 0$, i.e., when decomposition proceeds in vacuum, we obtain equation (5).

When $P_r^n > 0$, we obtain $q_1 > q_2 + nQ - \lambda$, and when $P_r^n = P_r^0$,

$$q_1 = \infty. \tag{11}$$

Consequently, depending on the initial gas pressure, the activation energy may vary from $q_2 + nQ - \lambda$ (5) to infinity.

To verify the conclusions set forth, we have studied in detail the kinetics of decomposition of cadmium carbonate in vacuum, at constant pressures of CO_2, different temperatures, and different supersaturations. The supersaturation and pressure during the reaction remained constant.

The results of our measurements after their processing are presented in Figs. 1 and 2. Each of the curves in Fig. 1 was obtained at constant pressure,

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

but at different temperatures, and each of the curves in Fig. 2 at constant supersaturation and different temperatures.

Table 1

P_{CO2}, mm	0	1.5	10	100	200	400	600	755
q, kcal/mol	36	65	68	77	85	107	140	160

P°_{CO2}/P_{CO2}	5	10	100	1000	10000
q, kcal/mol	39	43	43	36	36

The values of the activation energy calculated from the curves of Figs. 1 and 2 are given in Table 1. The data in the table are in complete agreement with

Fig. 1. Dependence of the logarithm of the rate constant of decomposition of cadmium carbonate on temperature at carbon dioxide pressures (mm Hg): 1—0; 2—1.5; 3—10; 4—100; 5—200; 6—400; 7—600; 8—755.

Fig. 2. Dependence of the logarithm of the rate constant of decomposition of cadmium carbonate on temperature at supersaturations.
P°_{CO2}/P_{CO2}: 1—5; 2—10; 3—100; 4—1000; 5—10 000.

the ideas set forth above. At the same time, they show that at supersaturations of 5-10 000 the reaction rate constants and activation energies found are not connected with crystallization processes, because the work of nucleus formation depends on the supersaturation, whereas the activation energy found by us does not depend on it.

Since crystallization processes in reversible reactions, in the range of the indicated supersaturations, have no effect on the rate constant and activation energy, still less should they exert an influence in irreversible topochemical reactions.

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