

## Concerning the Activation Energy of Solid State Reactions\*

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Determination of the activation energy of solid state reactions without account for changes in reagent imperfections leads to values of the energy of activation and the preexponential factor that are devoid of real physical significance. The behavior of reacting systems is investigated with the help of  $\ln k = f(1/T)$  diagrams for various lattice defect concentrations. A formula is derived which allows one to determine the solid state reaction rate constant for reacting systems with a constant concentration of lattice imperfections. Application of the derived equation is illustrated for the reaction  $\text{MgO} + \text{Fe}_2\text{O}_3$  with reagents of different thermal prehistory.

In connection with solid state reaction it is known that the idea of activation energy cannot be identified with the energy of the effective interaction of the particles. This is due in particular to the impossibility of distinguishing completely the given complex of particles that participate in an elementary act. Consequently, calculations of the activation energy carry a rather conventional character, and the value itself of the activation energy indicates in the optimal case only the degree of difficulty of the elementary steps of which the reaction is composed (1). Calculations of the activation energy as deduced from the formal linearized equation of Arrhenius,

$$k = k^0 \exp [-E/RT], \quad (1)$$

are in many cases not valid and do not take into account changes in the crystalline reagent structure that occur on going from one temperature to another (2).

In the present investigation an attempt was made to find the most correct way of calculating the value of the activation energy for a reaction involving a crystalline reagent (or

reagents). If these reagents are metal oxides, the rate constant of the reaction is given by

$$k = f(T, N, p_{\text{O}_2}); \quad (2)$$

that is, it depends not only on the temperature (in the case of gaseous reactions) but also on the concentration of reagent crystal lattice imperfections  $N$ , which in turn can be a well-defined function of the partial pressure of oxygen in the gas phase (case of equilibrium dissociation) or practically independent of  $p_{\text{O}_2}$  (nonequilibrium defects). The latter case is characteristic of a reaction involving active phases. Taking into consideration the fact that, in a crystal, precisely the lattice imperfections are the sites of the greatest possible realization of elementary acts, it would be correct to carry out the calculation of the activation energy by means of the equation

$$E = -R[d \ln k / d(1/T)]_N \quad (3)$$

that is, make use of the experimental dependence  $\ln k = f(1/T)$  at a fixed concentration of imperfections. Knowledge of  $E = f(N)$  would give sufficiently complete energetic characterization of the reaction.

However, in the majority of cases the activation energy of solid state processes is calculated by the equation

$$E = -R[d \ln k / d(1/T)]_{p_{\text{O}_2} = \text{const}}, \quad (4)$$

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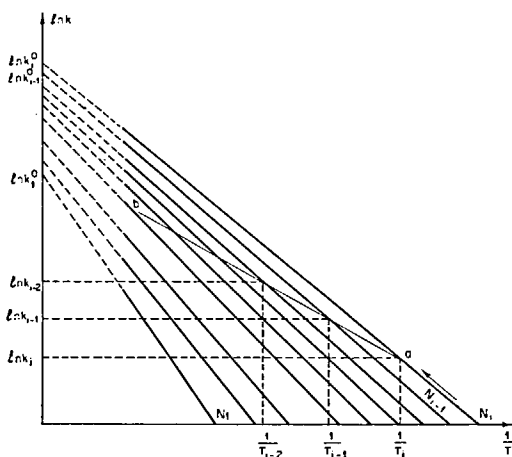


FIG. 1. Variation of  $\ln k$  with  $1/T$  for various concentrations of defects at a constant value of  $p_{O_2}$ .

ignoring the fact that for reactions with participation of active crystalline phases there occurs along with the process of reagent interaction an annealing of the imperfections of the crystal structure.

Let us consider the schematic diagram of Fig. 1 which characterizes the dependence of reaction rate constant on temperature for one and the same reaction at various concentrations of imperfections of a crystalline reagent (or reagents). The state with the minimal concentration of defects has corresponding to it the minimal value of the preexponential factor  $k_i^0$  (which characterizes the number of possible sites for generation of elementary acts of the interaction) and the maximum activation energy  $E_i = -R[d\ln k/d(1/T)]_{N_i}$ . Proportional to an increase in the defect character of the reagent crystal structure, the value of  $k_i^0$  must increase, whereas  $E_i$  decreases, thanks to which the curves  $\ln k = f(1/T)$  generate the unusual "fan" displayed in Fig. 1.

Let us consider the behavior of a mixture of crystalline reagents, the initial condition of which is characterized by some level of imperfections  $N_i$ . One can anticipate that, on heating, the reaction rate constant will change along an isoconcentration  $N_i$  (in the direction indicated by the arrow) as long as the crystal reagent defects are frozen in. Let us assume that at some temperature  $T_i$  appreciable

annealing of the defects begins so that at temperature  $T_{i-1}$  the concentration of defects amounts to  $N_{i-1}$ . However, at this level of imperfections the isoconcentration corresponds to a smaller value of the preexponential factor ( $k_{i-1}^0 < k_i^0$ ) and an increased activation energy ( $E_{i-1} > E_i$ ). Considering that with changing temperature the process of annealing of the imperfections in the crystalline reagents occurs uninterruptedly, one can expect that the values of the constants  $k_i, k_{i-1}, k_{i-2}$ , which are fixed experimentally at temperatures  $T_i, T_{i-1}, T_{i-2}$  correspond to different defect states and, hence, the quantities  $k^0$  and  $E$  calculated from these numbers are devoid of real physical significance.

In actuality, the annealing of imperfections makes solid state reactions more difficult, whereas the formal value of the activation energy as deduced from the straight line  $ab^1$  in Fig. 1 is markedly less than the real value of the activation energy including the one that characterizes to a maximum degree the defect state without breakup at the temperatures of the interaction.

The problem arises how to obtain the correct values of the activation energy that fully characterize distinct states of a given system. Assuming in the general case for a reaction involving crystalline oxides that the rate constant  $k = f(T, N, p_{O_2})$  can be written

$$d\ln k = \left( \frac{\partial \ln k}{\partial (1/T)} \right)_{N, p_{O_2}} d\frac{1}{T} + \left( \frac{\partial \ln k}{\partial n} \right)_{T, p_{O_2}} dN + \left( \frac{\partial \ln k}{\partial \ln p_{O_2}} \right) d\ln p_{O_2}, \quad (5)$$

differentiation of Eq. (5) with respect to  $1/T$  at  $p_{O_2} = \text{constant}$  gives

$$\left( \frac{\partial \ln k}{\partial (1/T)} \right)_{p_{O_2}} = \left( \frac{\partial \ln k}{\partial (1/T)} \right)_N + \left( \frac{\partial \ln k}{\partial N} \right)_T \left( \frac{\partial N}{\partial (1/T)} \right)_{p_{O_2}} \quad (6)$$

<sup>1</sup> In the general case the dependence  $\ln k = f(1/T)$  for simultaneous occurrence of 2 processes (interaction of reagents and annealing of imperfections out of the structure) should be curvilinear.

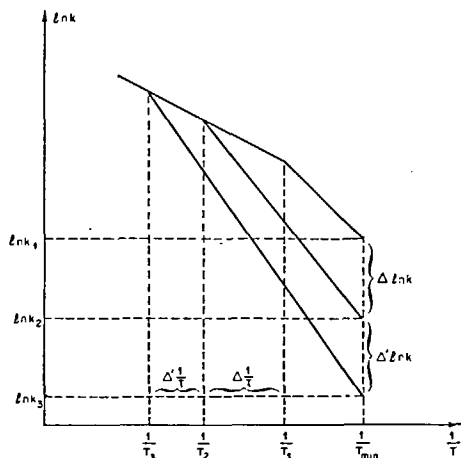


FIG. 2. Schematic drawing explaining the arrangement of experiments for determination of the activation energy by Eq. (7).

from which

$$\left(\frac{\partial \ln k}{\partial (1/T)}\right)_N = \left(\frac{\partial \ln k}{\partial (1/T)}\right)_{p_{O_2}} - \left(\frac{\partial \ln k}{\partial N}\right)_T \left(\frac{\partial N}{\partial (1/T)}\right)_{p_{O_2}} \quad (7)$$

Equation (7) allows one to calculate the activation energy of solid state reactions for the states of the crystalline reagents corresponding completely to a fixed concentration of imperfections. The data needed for the calculation are obtained in the following manner: The initial reagents are subjected appropriately to prolonged isothermal exposure at temperatures  $T_1, T_2, T_3$  and  $p_{O_2} = \text{const}$ ; then they are mixed and again heated at temperatures equal to the temperature of the heat treatment at  $p_{O_2} = p_{O_2}^0$ . Observation of the extent of reaction allows one to find values of  $k$  at various temperatures and to calculate  $[\partial \ln k / \partial (1/T)]_{p_{O_2}}$ . For evaluation of the second term in Eq. (7), the investigated reaction is carried out at a temperature considerably lower than the temperature of the preliminary heat treatment of the initial reagents, i.e.,  $T_{\min} \ll T_1 < T_2 < T_3$  (see Fig. 2). If one can assume that the concentration of imperfections in the starting reagents, fixed by the conditions of thermal treatment (at temperatures  $T_1, T_2, T_3 \dots$ ), does not change in the course of the chemical reaction, then

variations in  $\ln k$ , calculated for the solid phase reaction carried out at  $T_{\min}$  but with use of oxides first processed at  $T_1, T_2, T_3$ , etc., are dependent on variations in the concentrations of imperfections caused by the preliminary heat treatment.

This means that

$$\begin{aligned} \left(\frac{\partial \ln k}{\partial N}\right)_T \left(\frac{\partial N}{\partial (1/T)}\right)_{p_{O_2}^0} &\approx \frac{(\ln k_1 - \ln k_2)_{T_{\min}}}{(N_{T_1} - N_{T_2})_{T_{\min}}} \\ &\times \frac{(N_{T_1} - N_{T_2})_{p_{O_2}^0}}{(1/T_1 - 1/T_2)_{p_{O_2}^0}} \approx \frac{(\Delta \ln k)_{T_{\min}}}{\Delta(1/T)} \\ &\approx \frac{(\partial \ln k)_{T_{\min}}}{\partial (1/T)}. \end{aligned} \quad (8)$$

It is obvious that Eq. (8) is approximate, inasmuch as, strictly speaking, the concentration of imperfections  $N_1$  and  $N_2$ , fixed in the original oxides at  $T_1$  and  $T_2$ , respectively, ( $p_{O_2} = \text{const}$ ), can change somewhat under the conditions of the carrying out of the reaction.

Relation (8) was used for evaluation of the experimental data obtained in an investigation of the reaction of magnesium oxide with hematite that had differing thermal pretreatment (3). It was found that on carrying out the reaction in the interval 800–1000°C the activation energy at  $p_{O_2} = 0.21$  atm was approximately equal to 20 kcal/mole, whereas  $E_{N(900^\circ\text{C})} \approx 42$  kcal/mole and  $E_{N(1000^\circ\text{C})} \approx 70$  kcal/mole. The indices  $N(900^\circ\text{C})$  and  $N(1000^\circ\text{C})$  denote that the concentrations of the imperfections in the initial reagents were fixed by prolonged preheating at the corresponding temperatures. As was to be expected, the value of the activation energy at  $p_{O_2} = 0.21$  atm is markedly lower than the activation energy at  $N = \text{const}$ , and the latter value increases proportionally to the value of the temperature of the preliminary working, approaching the magnitude of the activation energy for volume diffusion of  $\text{Fe}^{3+}$  ions in the spinel lattice,  $E_D = 75$  kcal/mole (4).

An analogous analysis can be carried out for the case where, on temperature increase, the concentration of defects that limits the interaction of crystalline reagents increases as a result of natural atomic disordering or of a change in the nonstoichiometry of the initial oxides or the products of the reaction,

Equation (7) can be represented in the following way:

$$\begin{aligned} \left(\frac{\partial \ln k}{\partial(1/T)}\right)_N &= \left(\frac{\partial \ln k}{\partial(1/T)}\right)_{p_{O_2}} - \left(\frac{\partial \ln k}{\partial \ln p_{O_2}}\right)_T \\ &\quad \times \left(\frac{\partial \ln p_{O_2}}{\partial N}\right)_T \left(\frac{\partial N}{\partial(1/T)}\right) \\ &= \left(\frac{\partial \ln k}{\partial(1/T)}\right)_{p_{O_2}} - \frac{\left(\frac{\partial \ln k}{\partial \ln p_{O_2}}\right)_T \left(\frac{\partial N}{\partial(1/T)}\right)}{\left(\frac{\partial N}{\partial \ln p_{O_2}}\right)_T} \end{aligned} \quad (9)$$

On use of Eq. (9) for treatment of the experimental data that characterize the interaction in  $MgO + Fe_2O_3$  mixtures at 1000–1300°C (5), the following results were obtained<sup>2</sup>:

$$\begin{aligned} E_{p_{O_2}} &= 120 \text{ kcal/mole,} \\ E_{N(1000^\circ C)} &\approx 105 \text{ kcal/mole,} \\ E_{N(1100^\circ C)} &\approx 100 \text{ kcal/mole,} \\ E_{N(1200^\circ C)} &\approx 90 \text{ kcal/mole,} \\ E_{N(1300^\circ C)} &\approx 80 \text{ kcal/mole,} \end{aligned}$$

where indices of the type  $N(1000^\circ C)$  denote the temperature of the preliminary working of the pure reagents. The decreasing activation energy for ferrite formation found at higher temperatures of preliminary working can be

<sup>2</sup> For calculations of the separate individual derivatives, the data of Ref. (6) were used.

attributed to the increase in defect character of the starting oxides.

### Conclusions

Possible errors in the determination of the activation energy of solid state reactions involving crystalline reagents are analyzed. Equations are derived for proper evaluation of the activation energy at a fixed concentration of imperfections in the crystal lattice of the reagents. Examples illustrating the effectiveness of the proposed methods of treating experiments are discussed.

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