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FACTORS ON WHICH THE RATE OF SOLID–SOLID REACTIONS DEPENDS

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ABSTRACT

The results of an investigation of the influence of the molar ratio of the reactants, the degree of compactness, and the ratio of the mean radii of the grains on the rate of solid–solid reactions are presented. The theoretical curves, generated with a computer using a BASIC program by assuming that the limiting step is nucleation at the contact surface, are compared with the experimental data for the reaction between $BaCl_2$ and KNO_3.

INTRODUCTION

In a previous paper [1], a kinetic model for solid–solid reactions of the form was presented

I: $A_{(s)} + B_{(s)} \rightarrow cC_{(s)} + dD_{(s)}$

The corresponding corrected rate equation is:

$$v = \frac{d\alpha}{dt} = \frac{8\pi\gamma r_A h P_0 n_1}{1+R'} e^{-E/RT}\left\{1 + \frac{r_A}{r_0\left[1+\left(\frac{r_f}{r_0}-1\right)\alpha\right]}\right\}^2 (1-q\alpha)(1-\alpha) \tag{1}$$

where α is the degree of conversion with respect to the limiting reactant A, γ is the degree of compactness of the sample, h is the height of the contact spherical segment between grains, P_0 is the frequency factor, n is the number of nuclei in the surface unit, E is the activation energy, R is the gas constant, T is the temperature (in Kelvin), r_A is the mean radius of the grains for reactant A, and r_0 and r_f are the mean radii of the sample at the beginning and the end of the reaction, respectively.

The ratios R' and q are defined as

$$R' = \frac{m_A^0}{m_B^0}\left(\frac{r_B}{r_A}\right)^3\left(\frac{\rho_B}{\rho_A}\right) \tag{2}$$

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$$q = \frac{bM_Bm_A^0}{M_Am_B^0} \tag{3}$$

where m_A^0 and m_B^0 are the initial masses of the reactants A and B in the mixture, M_A and M_B are the molecular weights of A and B, ρ_A and ρ_B are the densities of A and B, r_A and r_B are the mean radii of A and B, and b is the stoichiometric ratio

Equation (1) was used to evlauate the activation energy of the reaction between $BaCl_2$ and KNO_3 [2].

In the following the change in the form of the kinetic curves with the molar ratio of the reactants, the degree of sample compactness, and the ratio $p = r_0/r_f$ is discussed.

RESULTS AND DISCUSSION

The theoretical curves were generated using a program written in BASIC [3], which was run on a TIM-S computer. The differential thermal analysis (DTA) curve for the reaction

II: $BaCl_2 + 2KNO_3 = Ba(NO_3)_2 + 2KCl$

was recorded using a Q-MOM Budapest Paulik, Paulik, Erdey, derivatograph.

The influence of the molar ratio of the reactants on the reaction rate

The simple case for which $r_A = r_B = r$ is considered. From eqns. (2) and (3),

$$R' = \frac{qM_A\rho_B}{bM_B\rho_A}$$

Taking into account this result, eqn. (1) becomes

$$v = \frac{32\pi\gamma rhP_0n_1\,\mathrm{e}^{-E/RT}}{1 + \dfrac{qM_A\rho_B}{bM_B\rho_A}}(1 - q\alpha)(1 - \alpha) \tag{4}$$

for $r_f/r_0 = 1$.

Introducing the notation

$$A = 32\pi\gamma rhP_0n_1\,\mathrm{e}^{-E/RT}$$

and

$$B = \frac{M_A\rho_B}{bM_B\rho_A} \tag{5}$$

one obtains

$$V = \frac{A}{1 + Bq}(1 - q\alpha)(1 - \alpha) \tag{6}$$

and for the molar ratio it is suitable to use the parameter q which is a stoichiometric molar ratio

$$q = \frac{\nu_B/\nu_A}{n_B/n_A} \tag{7}$$

where $\nu_B = b$, $\nu_A = 1$, $n_B = m_B^0/M_B$ and $n_A = m_A^0/M_A$.

For a sample which contains the reactant A in infinite dilution, $(q \rightarrow 0)$ the initial $(\alpha \rightarrow 0)$ reaction rate, v_0, can be expressed as

$$v_0 = A \tag{8}$$

The relative reaction rate v_r is defined as

$$v_r = \frac{v}{v_0} = \frac{(1 - q\alpha)(1 - \alpha)}{1 + Bq} \tag{9}$$

In this relationship $0 \leqslant \alpha \leqslant 1$, $0 \leqslant q \leqslant 1$ and $0 \leqslant v_r \leqslant 1$. For reaction **II**, $b = 2$, $\rho_A = \rho_{BaCl_2} = 3.911$ g cm^{-3} and $\rho_B = \rho_{KNO_3} = 3.109$ g cm^{-3}. One obtains $B = 0.556$. Thus eqn. (9) takes the form

$$v_r = \frac{(1 - q\alpha)(1 - \alpha)}{1 + 0.556q} \tag{10}$$

The curves $v_r = f(q(i), \alpha)$ were generated using eqn. (10). The curves v_r, α for $q(1) = 0$, $q(2) = 0.4$ and $q(3) = 1$ are given in Fig. 1. It can be seen from Fig. 1 that the maximum value of the reaction rate is recorded for an infinite dilution $(q \rightarrow 0)$. Under such conditions the probability of contact between a grain of A and a grain of B tends to unity. Equation (9), with the condition $q \rightarrow 0$, gives $v_r = 1 - \alpha$, which shows that the reaction rate is directly proportional to the amount of limiting reactant. This result is in accordance with the degeneracy of the reaction order observed in homogeneous kinetics when one reactant is in excess.

The dependence $v_r = f(\alpha(i), q)$ for various values of the degree of conversion is shown in Fig. 2.

The values of the reaction rate, obtained from the DTA curves by extrapolating $\alpha \rightarrow 0$, gave the linear theoretical curve (a) shown in Fig. 2.

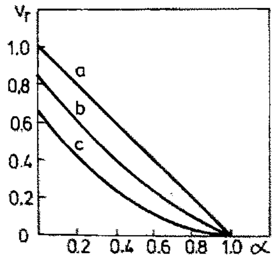

Fig. 1. Curves $v_r = f(q(i), \alpha)$: (a) $q(1) = 0$; (b) $q(2) = 0.4$; (c) $q(3) = 1.5$.

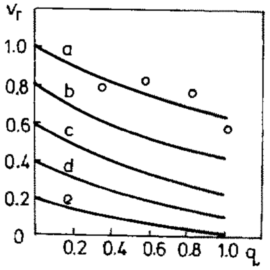

Fig. 2. Curves $v_r = f(\alpha(i), q)$: (a) $\alpha(1) = 0$; (b) $\alpha(2) = 0.2$; (c) $\alpha(3) = 0.4$; (d) $\alpha(4) = 0.6$; (e) $\alpha(5) = 0.8$.

The experimental values were normalized with respect to the maximum value obtained through the extrapolation of $q \to 0$.

The influence of the degree of compactness of the powdered samples on the reaction rate

The degree of compactness has been defined through the ratio between the true volume of the reactants and the apparent volume of the sample:

$$\gamma = \left(\frac{m_A^0}{\rho_A} + \frac{m_B^0}{\rho_B} \right) / V_a$$

For the sake of simplicity, the reaction rate is normalized with respect to v_0' (the initial reaction rate corresponding to a sample which consists of spherical grains with a degree of compactness of 0.74).

By introducing in eqn. (1) the conditions $\alpha = 0$, $\gamma = 0.74$ and $r_A = r_B = r_f = r_0 = r$, one obtains

$$v_0' = \frac{32\pi 0.74 r h P_0 n_1 \, e^{-E/RT}}{1 + R'} \tag{11}$$

The normalized reaction rate is obtained from the ratio between eqn. (1) with $r_A = r_f = r_0$ and $q = 1$ and eqn. (11)

$$v_r' = \frac{v}{v_0'} = \frac{\gamma(1-\alpha)^2}{0.74} \tag{12}$$

The curves $v_r' = f(\gamma(i), \alpha)$ were generated using eqn. (12) (Fig. 3). The set of straight lines $v_r' = f(\alpha_A(i), \gamma)$ are given in Fig. 4. Note that the influence of the degree of compactness is significant at low values of the degree of conversion. According to eqn. (12), the maximum value of the slope (1/0.74) for the straight lines $v_r' = f(\gamma)$ is obtained when $\alpha = 0$.

The experimental values of the relative reaction rate are also given in Fig. 4. These data were normalized with respect to the reaction rate corresponding to a sample having a degree of compactness of 0.74. As it was not possible to obtain samples with $\gamma = 0.74$, the corresponding reaction rate

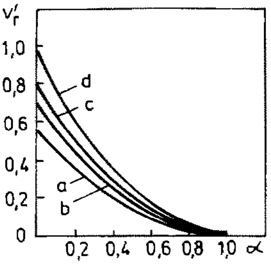

Fig. 3. Curves $v_r' = \mathrm{f}(\gamma(i), \alpha)$: (a) $\gamma(1) = 0.4$; (b) $\gamma(2) = 0.5$; (c) $\gamma(3) = 0.6$; (d) $\gamma(4) = 0.74$.

was also evaluated by extrapolation of the experimental data. In this range the reaction rate can be considered to be linearly dependent on the degree of compactness of the sample.

The dependence of the reaction rate on the ratio $p = r_f/r_0$

The model was developed by assuming that during the solid–solid reaction the number of grains remains constant. As the weight of the system remains constant, it can be concluded that the mean weight of the sample grains also remains constant. Nevertheless, the initial value of the radius of the crystalline grains, r_0, differs from the corresponding final value, r_f, due to the difference in density between reactants and products. Thus,

$$p = \frac{r_f}{r_0} = \left(\frac{\rho_0}{\rho_f}\right)^{1/3} \tag{13}$$

The ratio p can be determined either by granulometric analysis or by measuring the densities ρ_0 and ρ_f. Another possibility consists in evaluating the mean density of the sample from the densities of the solid phases involved in the reaction.

For the sake of simplicity, consider a sample whose weight equals 1 g. In such conditions the weights W_A and W_A of reactants are identical to the

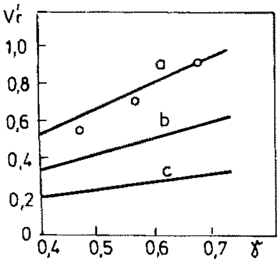

Fig. 4. Curves $v_r' = f(\alpha(i), \gamma)$: (a) $\gamma(1) = 0$; (b) $\alpha(2) = 0.2$; (c) $\gamma(3) = 0.4$.

corresponding weight fractions. The volume of the sample is then evaluated by summing the volumes of the two phases.

The mean density is given by

$$\rho_0 = \frac{1}{W_A/\rho_A + (1 - W_A)/\rho_B} \tag{14}$$

and if the reaction goes to completion

$$\rho_f = \frac{1}{W_C/\rho_C + (1 - W_C)/\rho_C} \tag{15}$$

According to the stoichiometric equation **I**, $W_C = W_A c M_C / \mathrm{M}_A$. Thus it is possible to express the densities ratio using only one weight fraction, i.e. that of the limiting reactant A,

$$\frac{\rho_0}{\rho_f} = \frac{\rho_A \rho_B \left[M_A \rho_C + W_A c M_C (\rho_D - \rho_C) \right]}{\rho_C \rho_D M_A \left[\rho_A + W_A (\rho_\beta - \rho_A) \right]} \tag{16}$$

Using the literature data concerning the density of the solid phases from reaction **II** one obtains $\rho_0/\rho_f = 1.028$ and, using eqn. (13), $p = 1.085$.

The value $p = 1.102$ was obtained by means of the pycnometric method. The higher value obtained can be explained taking into account the fact that the reaction products are characterised by an imperfect structure and thus by a lower density than that of the pure crystalline phases. When using this method the samples should be moderately heated to avoid sintering of the grains.

Thus, the ratio p has little influence on the form of the kinetic curves for reaction **II**. To illustrate the influence of this parameter, consider three hypothetical solid–solid reactions for which $p(1) = 1/10$, $p(2) = 1$ and $p(3) = 10$.

The reaction rate is normalized with respect to the rate corresponding to a sample with stoichiometric composition and with $r_f = r_0 = r_A$. One obtains succesively

$$v_0'' = \frac{32\pi\gamma r_0 h P_0 n_1}{1 + R'} \cdot e^{-E/RT} \tag{17}$$

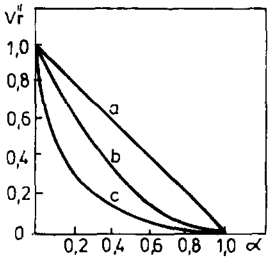

Fig. 5. Curves $v'' = f(p(i), \alpha)$: (a) $p(1) = 1/10$; (b) $p(2) = 1$; (c) $p(3) = 10$.

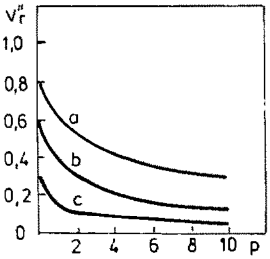

Fig. 6. Curves $v_r'' = f(\alpha(i), p)$: (a) $\alpha(1) = 0.2$; (b) $\alpha(2) = 0.4$; (c) $\alpha(3) = 0.6$.

$$v = \frac{v}{v_0''} = \frac{1}{4}\left\{1 + \frac{1}{[1 + (p-1)\alpha]}\right\}^2 (1-\alpha)^2 \qquad (18)$$

The curves $v'' = f(p(i), \alpha)$ expressing the dependence of the normalized reaction rate on the degree of conversion for the three values of p considered are shown in Fig. 5. The curves $v'' = f(\alpha_A(i), p)$ for the change of the reaction rate with p for the three values of the degree of conversion are presented in Fig. 6. Inspection of these results shows that the reaction rate is lower in the systems characterised by high values of p. The explanation of this fact consists in the decrease in the probability of contact of the two reactants due to the lower density and thus higher volume of the products with respect to the reactants.

CONCLUSIONS

The kinetic curves generated in this work show that the present model describes the sensitivity of the solid–solid reaction to the ratio of reactants and the degree of compactness of the sample. These observations were confirmed by the kinetic behaviour of the system, $BaCl_2/KNO_3$.

Taking into account that the ratios between the mean densities of the reactants and the mean densities of the products are close to unity, it follows that this parameter has little influence on the reaction rate and on the form of the kinetic curves.

The theoretical curves show a decrease in reaction rate with increasing ratio r_f/r_0.

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