Thermochimica Acta, 131 (1988) 65–71
Elsevier Science Publishers B V , Amsterdam – Printed in The Netherlands

KINETIC MODELS FOR SOLID–SOLID REACTIONS

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(Received 9 November 1987)

ABSTRACT

The author develops two kinetic models for the reactions given by the chemical equation $a\mathrm{A(s)} + b\mathrm{B(s)} \rightarrow c\mathrm{C(s)} + d\mathrm{D(s)}$ occurring in powdered samples One of the models deals with reactions limited by the nucleation on contact surfaces between grains, the other one with reactions limited by crystallization of products C and D What is novel is taking into account the dispersion degree of reactants and the settling degree of the sample as well as the change of the mean grain radius with the conversion degree

INTRODUCTION

Reactions which include solid reactants are very complex from the kinetic standpoint, as they involve several physical and chemical steps [1] Another peculiarity of solid state reactions is their sensitivity to the previous mechanical and thermal treatments of the samples [2,3] The two models given in this paper take into account these peculiarities

Let us consider a solid–solid reaction described by the general stoichiometric equation

$$a'\mathrm{A(s)} + b'\mathrm{B(s)} \rightarrow c'\mathrm{C(s)} + d'\mathrm{D(s)} \tag{1}$$

where A is the limiting reactant By dividing by a', equation (1) becomes

$$\mathrm{A(s)} + b\mathrm{B(s)} \rightarrow c\mathrm{C(s)} + d\mathrm{D(s)} \tag{2}$$

where $b = b'/a'$, $c = c'/a'$, and $d = d'/a'$ The following steps of the reaction will be considered

(1) The interaction of the reactants A and B at the contact surface between grains with the appearance of the new phases A and B nuclei

(2) The growth of the nuclei due to the diffusion of mobile particles through the solid products layer

(3) The crystallization of the reaction products

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NUCLEATION AS THE LIMITING STEPS

The rate equation will be derived taking into account the following assumptions·

(a) The nucleation rate for the stable nuclei dN/dt is directly proportional to the total interaction surface S between reactants grains, and to the potential nuclei on unit surface The proportionality constant P has the meaning of a probability of transformation of a potential nucleus into a stable one in unit time Thus

$$\frac{dN}{dt} = Pn_1S \tag{3}$$

where N is the number of stable nuclei which have appeared at the moment t

(b) The probability P, which has the meaning of a rate constant, is given by the Arrhenius equation

$$P = P_0\, e^{-E/RT} \tag{4}$$

where P_0 is the pre-exponential factor ($P_0 \approx 10^{13}$ s^{-1})

(c) The interaction surface corresponding to a contact between two grains of the reactants A and B will be considered as equal to the surface of the segment of height h (Fig 1) The particles on the two surfaces separated by a distance greater than $2h$, ($d > 2h$) cannot interact to form stable nuclei The distance $2h$ is of the order of magnitude of the parameter of crystalline cell ($2h \approx 10$ Å)

(d) For the integral conversion of the limiting reactant A grain, the appearance of only one nucleus on the surface s is sufficient

(e) The number of grains remains constant during the reaction. The interaction of two reactant grains leads to two grains composed from the products C and D and the excedentary reactant B (Fig 1). Thus the conservation law of the number of grains is

$$n_A^0 + n_B^0 = n_t = \text{const} \tag{5}$$

where n_A^0 is the initial number of grains of the reactant A, n_B^0 the

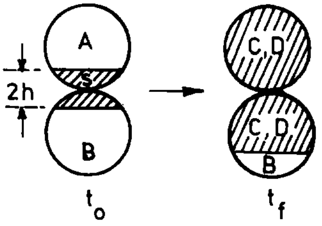

Fig 1 Grains A and B leading to reaction products C and D at initial time t_0, t_f is the final time, s is the interaction surface corresponding to a contact AB, $2h$ is the maximal distance of interaction, B is the excedentary reactant, and A is the limiting reactant

corresponding number for the reactant B, and n_t the constant total number of grains at any moment.

As the reaction occurs without evolution of gas the mass of the reacting system is constant Thus

$$m_A^0 + m_B^0 = m = \text{const} \tag{6}$$

The ratio m/n_t which represents the mean mass of the grain is also constant Nevertheless the mean radius of the grains changes during the reaction as the density of the products differs from the density of the reactants.

(f) The mean radius r of the solid grains changes with the conversion degree α_A according to the relationship

$$r = a + b\alpha_A \tag{7}$$

At the initial moment $\alpha_A = 0$ and $r = r_0$, r_0 being the mean radius of the grains from the initial mixture of reactants At the end of the reaction $\alpha_A = 1$ and $r = r_f$, r_f being the mean radius of the grains from the final mixture of product C and D and excedentary reactant B Taking into account the conditions from eqn (7) one obtains $a = r_0$, $b = r_f - r_0$ and

$$r = r_0\left[1 + \left(\frac{r_f}{r_0} - 1\right)\alpha_A\right] \tag{8}$$

(g) The number of contacts between one grain and the surrounding ones is directly proportional to the compactness factor γ of the sample defined by the relationship

$$\gamma = \frac{\dfrac{m_A^0}{\rho_A} + \dfrac{m_B^0}{\rho_B}}{V_a} \tag{9}$$

where ρ_A and ρ_B stand for the density of reactants A and B. The numerator contains the true volume of the reactants, the denominator contains the volume of the crucible occupied by the powdered reaction mixture

One assumes that the compactness factor does not change during the reaction, and that this factor depends only on the settling degree of the sample at the initial moment As nucleation is the limiting step, the reaction rate is given by eqn (3) The conversion degree is given by the obvious relationship

$$\alpha_A = \frac{m_A}{m_A^0} \tag{10}$$

where m_A is the weight of the reactant transformed at time t

According to assumption (d), each of the N stable nuclei turned into products a grain of the reactant A with the mean weight M_{A1} Thus the mass of the transformed limiting reactant can be expressed by $m_A = Nm_{A1}$ and eqn (10) becomes

$$\alpha_A = \frac{Nm_{A1}}{m_A^0} \tag{11}$$

The mean mass of the grains can be calculated from the mean radius r_A^0 determined by granulometric analysis of the reactant A prior to mixing. If one assumes a spherical shape for the grains one obtains

$$m_{A1} = \frac{4\pi\left(r_A^0\right)^3 \rho_A}{3} \tag{12}$$

From eqn (11), taking the derivative with respect to time

$$\frac{d\alpha_A}{dt} = \frac{m_{A1}}{m_A^0}\frac{dN}{dt} \tag{13}$$

Taking into account eqns (1) and (2), eqn (13) becomes

$$\frac{d\alpha_A}{dt} = \frac{P_0 m_{A1} m_1}{m_A^0}\left(e^{-E/RT}\right)S \tag{14}$$

The interaction surface S depends on α_A To derive the analytical form of such a dependence, a grain of A surrounded by other spherical grains will be considered (Fig. 2)

The number of contacts $C_{A1,i}$ among a grain A and all the other grains i (i = A, B, C, D) is directly proportional to the settling degree of the sample r, and to the ratio between the area of the contact sphere with radius $r_A + r$ (the broken circle in Fig 2) and the area of the mean section $S_i = \pi r^2$ of the surrounding spheres Thus

$$C_{A1,i} = 4K\gamma\left(1 + \frac{r_A}{r}\right)^2 \tag{15}$$

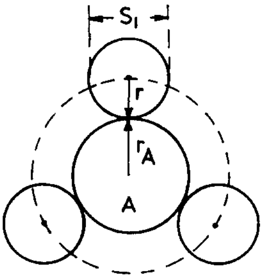

Fig 2 Simplified model of the contacts between a grain of the reactant A and the other grains from the system considered as spheres of main radius r

The constant K can be calculated taking into account that for a compact model with spheres of equal radius the following conditions are fulfilled $r_A = r$, $\gamma = 0.74$, $C_{A1,i} = 12$. Introducing these values in eqn (15) one obtains

$$K = 1 \tag{16}$$

For the occurrence of the reaction, only the number of the contacts $C_{A1,B}$, between the grain A and the grains B are important. Obviously this number is given by

$$C_{A1,B} = C_{A1,i} X_B \tag{17}$$

where X_B is the fraction of the number of grains of B.

Taking into account this definition and assumption (e) one obtains

$$X_B = \frac{n_B}{n_A^0 + n_B^0} = \frac{\dfrac{m_B^0(1-\alpha_B)}{m_{B,1}}}{\dfrac{m_A^0}{m_{A,1}} + \dfrac{m_B^0}{m_{B,1}}} = \frac{1 - q\alpha_A}{1 + R} \tag{18}$$

where

$$R = \frac{m_B^0 m_{A1}}{m_A^0 m_{B1}} = \frac{m_B^0}{m_A^0}\left(\frac{r_A^0}{r_B^0}\right)^3\left(\frac{\rho_A}{\rho_B}\right) \tag{19}$$

$$q = \frac{\alpha_B}{\alpha_A} = \frac{bM_B}{M_A}\,\frac{m_A^0}{m_B^0} \tag{20}$$

α_B is the conversion degree with respect to reactant B, and M_A and M_B are the molar weights of the reactants A and B.

Taking into account eqns. (15), (16) and (18), one obtains from eqn (17)

$$C_{A1,B} = 4\gamma\left(1 + \frac{r_A}{r}\right)^2\left(\frac{1 - q\alpha_A}{1 + R}\right) \tag{21}$$

The total number of contacts $C_{A,B}$ between the grains A and B can be obtained from $C_{A1,B}$ through multiplication by n_A (the number of A grains).

Because $n_A = m_A^0(1 - \alpha_A)/m_{A1}$ one obtains

$$C_{A,B} = \frac{C_{A1,B}\, m_A^0(1-\alpha_A)}{m_{A,1}} \tag{22}$$

The total contact surface can be obtained from the number of contacts $C_{A,B}$ and the surface $s = 2\pi r_A h$ of the segment of the grain A

$$S = 2\pi r_A C_{A,B} \tag{23}$$

With this result eqn (14) becomes

$$\frac{d\alpha_A}{dt} = \frac{2\pi\gamma r_A h P_0 m_{A1} n_1}{m_A^0}\left(e^{-E/RT}\right) C_{A,B} \tag{24}$$

or, taking into account eqns (8), (21) and (22)

$$\frac{\mathrm{d}\alpha_{\mathrm{A}}}{\mathrm{d}t}=\frac{8\pi\gamma r_{\mathrm{A}}hP_0n_1}{1+R}\left\{\mathrm{e}^{-E/RT}1+\frac{R_{\mathrm{A}}}{r_0\left[1+\left(\frac{r_{\mathrm{f}}}{r_0}-1\right)\alpha_{\mathrm{A}}\right]}\right\}(1-q\alpha_{\mathrm{A}})(1-\alpha_{\mathrm{A}}) \tag{25}$$

For $r_0=r_{\mathrm{f}}=r$, $r_{\mathrm{A}}=r_{\mathrm{B}}=r_0=r$ and a stoichiometric mixture of reactants $(m^0_{\mathrm{A}}/m^0_{\mathrm{B}})(M_{\mathrm{B}}/M_{\mathrm{A}})=1/b$, $q=1$, $\alpha_{\mathrm{A}}=\alpha_{\mathrm{B}}$, eqn (25) becomes its simplified variant

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=\frac{32\pi\gamma rhP_0n_1}{1+R}(\mathrm{e}^{-E/RT})(1-\alpha)^2 \tag{28}$$

This equation corresponds formally to a second-order reaction

CRISTALLIZATION AS THE LIMITING STEP

In this case the nucleation occurs not only on the surface, but also in the bulk of the amorphous phase Thus

$$\frac{\mathrm{d}N}{\mathrm{d}t}=P_0(\mathrm{e}^{-E/RT})n_1V \tag{29}$$

where n_1 is the number of potential cristallization nuclei in the volume unit, V is the volume of the amorphous phase at time t, N is the number of stable crystallization nuclei, and P_0 is the pre-exponential factor

Obviously

$$\alpha=\frac{V_0-V}{V_0} \tag{30}$$

where V_0 is the initial volume or amorphous product.

Assuming that each nucleus from the N stable nuclei leads through growth to the crystallization of a mean volume V_1 of amorphous product, the difference V_0-V_1 (the volume of amorphous product which has crystallized) can be replaced by V_1N Thus

$$\alpha=\frac{V_1N}{V_0} \tag{31}$$

Taking the derivative of α with respect to time we obtain

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=\frac{V_1}{V_0}\frac{\mathrm{d}N}{\mathrm{d}t} \tag{32}$$

Taking into account eqn (29), eqn. (32) becomes

$$\frac{d\alpha}{dt} = \frac{P_0 n_1 V_1}{V_0}(e^{-E/RT})V \tag{33}$$

From eqns. (30) and (33) it follows that

$$\frac{d\alpha}{dt} = P_0 n_1 V_1 (e^{-E/RT})(1 - \alpha) \tag{34}$$

The equations of the reaction rate could be used either in differential or in integral form for isothermal or non-isothermal conditions [4,5]

A subsequent paper will show how the above considerations are confirmed by the kinetics of the reaction [6]

$$BaCl_2(s) + 2KNO_3(s) \rightarrow Ba(NO_3)_2 + 2KCl \tag{35}$$

CONCLUSIONS

Two kinetic models describing solid-solid reactions were developed The first model takes into account the dispersion degree and the settling degree of the reactants, as well as the change of the grain mean radius with conversion.

The models presented allow the calculation of the pre-exponential factor

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