

## MODELLING OF DIFFUSION-CONTROLLED SOLID-SOLID REACTIONS

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A model describing the initial step of diffusion-controlled solid-solid reactions is presented. The kinetic equation obtained was used to evaluate the activation energy of the reaction  $\text{LiCl(s)} + \text{NaF(s)} = \text{LiF(s)} + \text{NaCl(s)}$  from DTA data.

**Keywords:** kinetics, solid-solid reactions

### Introduction

The kinetic models of Jander and Ginsting-Brounshtein [1] frequently used to describe solid-solid reactions, take into account the total coverage of the crystalline grains of one reactant with the mobile particles of the other one, with the generation of a unique reaction front.

In the following a model based on the generation of several reaction fronts localised at the contact points between the crystalline grains of the reactants is presented.

### Kinetic equations

The derivation of the kinetic equation is based on the following assumptions:

- a) The reaction  $\text{A(s)} + \text{B(s)} \rightarrow \text{P(s)}$  is limited by the diffusion of the mobile particles of the reactant B into the bulk of reactant A grains;
- b) The mean diffusion distance is expressed by the relationship [2]

$$d = f t \delta^2$$

$$d = (6 D t)^{1/2} \quad (1)$$

where  $D=f\delta^2/6$  is the diffusion coefficient,  $f$  – jump frequency of mobile ions,  $\delta^2$  – mean square distance of one jump.

c) The total volume of the reaction products  $P(s)$  does not differ appreciably from the total volume of the reactants;

d) In the initial period of the reaction the average number of contacts  $C_{A,B}$  between a grain of A and the grains of B (assimilated by spheres) is constant and the diffusion fronts emerging from them do not overlap to a significant extent:

e) The limiting reactant is A.

The reaction products corresponding to the contact point B are generated at the intersection of the diffusion sphere (of variable radius  $d$ ) and the spherical grain A (Fig. 1).

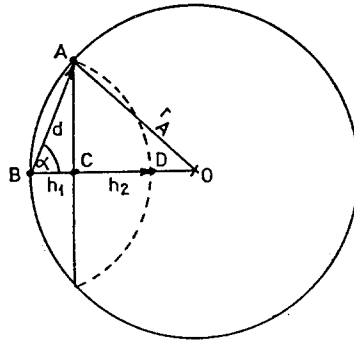


Fig. 1 The spherical diffusion front (---) in the grain of the reactant A

Thus, the volume  $v_1$  of the transformed reactant A is calculated by the summation of the volumes of the two spheric segments with the heights  $h_1=BC$  and  $h_2=CD$  and radii  $r_A$  and  $d$  respectively:

$$v_1 = \frac{\pi}{3} \left[ h_1^2(3r_A - h_1) + h_2^2(3d - h_2) \right] \quad (2)$$

From the triangles ABC and ABO one obtains:

$$h_1 = d \cos \alpha = \frac{d^2}{2r_A} \quad (3)$$

$$h_2 = d - h_1 = \frac{d(2r_A - d)}{2r_A} \quad (4)$$

The degree of conversion of the grain A is calculated from the ratio of the total volume  $C_{A,B}V_1$  and the volume of the grain A:

$$\alpha = \frac{C_{A,B}V_1}{4r_A^3} \quad (5)$$

Taking into account relationships (2)–(5) it turns out that:

$$\alpha = \frac{C_{A,B}}{16} \left( \frac{d}{r_A} \right)^3 \cdot \left( B - 3 \frac{d}{r_A} \right) \quad 0 \leq d \leq l \quad (6)$$

Relationship (6) permits to calculate the degree of conversion until the moment when the diffusion spheres which start in various points  $B_1, B_2, \dots$  (Fig. 2) come into contact and their mean radius reaches its extreme value for  $d=l$ .

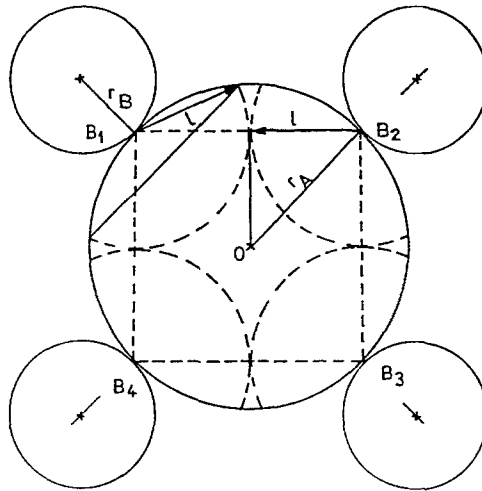


Fig. 2 The geometric model of grain packing for  $C_{A,B}=6$

In order to estimate the limit value  $\alpha_1$  which could still be calculated by relationship (6) let us consider a sample which consists of spherical grains with  $r_A=r_B=r$ , compactness factor  $\gamma=3/4$  and with the fraction of the grain number  $X_A=X_B=1/2$ . The average number  $C_{A,B}$  of grains from reactant B which surround a grain from the reactant A can be calculated [3] according to the relationship (7):

$$C_{A,B} = 4\gamma \left( 1 + \frac{r_A}{r} \right)^2 X_B \quad (7)$$

One obtains  $C_{A,B}=6$ . The grains of the reactants A and B which surround a grain from the reactant A are randomly distributed. In order to evaluate the distance  $l$ , the most symmetrical distribution in which the grain A is located in the center of an octahedron and six B in its vertices will be considered (Fig. 2).

From the geometry of the octahedron one obtains  $l=(r_A^2/2)^{1/2}$ . These results lead to  $\alpha_1=0.78$ . If the reactant B is in excess ( $X_B \rightarrow 1$ ) then  $C_{A,B}=12$ . From the twelve grains of the reactant B which surround the grain A, six lie in the same plane with it and the most uniform distribution of the contact points corresponds to the vertices of a hexagon.

In this case,  $l=r_A$  and  $\alpha_1=0.61$ . For  $d>l$  the areas of the diffusion fronts which intersect could be assimilated to an envelope spherical area which corresponds to the Ginsting-Brounshtein model.

The most unfortunate case corresponds to a sample for which  $X_B \gg X_A$  and  $r_B \ll r_A$ . In this case, the grain A is surrounded by many small grains and the interaction of the diffusion fronts begins from the initial reaction time. Thus the applicability field of Eq. (6) is determined by the fraction of the number of grains as well as by the ratio of the mean grain radii.

From relationships (1) and (6) one obtains:

$$\frac{\alpha}{t^{3/2}} = B - Gt^{1/2} \quad (8)$$

where

$$B = \frac{8C_{A,B}(6D)^{3/2}}{r_A^3}; \quad G = \frac{3C_{A,B} \cdot 6^{3/2} D^2}{r_A^4}$$

The applicability field of Eq. (8) could be checked from the dependence ( $\alpha/t^{3/2}$  vs.  $t^{1/2}$ ) which should be linear for the initial moments of the reaction. For small values of the time  $Gt^{1/2} \ll B$  and relationship (8) takes the simplified form:

$$\alpha = Bt^{3/2} \quad (9)$$

The rate equation can be obtained from (9) taking the derivative with respect to time:

$$\frac{d\alpha}{dt} = \frac{3}{2} B^{2/3} \alpha^{1/3} \quad (10)$$

In nonisothermal conditions the constant B depends on the temperature through the diffusion coefficient  $D$ .

Taking into account that:

$$D = D_0 e^{-E/RT} \quad (11)$$

where all the notations have known meanings one obtains:

$$\frac{1}{\alpha^{1/3}} \frac{d\alpha}{dt} = Z e^{-E/RT} \quad (12)$$

where

$$Z = \frac{36 C_{A_1 B}^{3/2} \cdot D_0 \cdot e^{-E/RT}}{r_A^2}$$

The occurrence of solid-solid reactions can be followed with the help of a DTA experiment. In such conditions:

$$\alpha = \frac{a}{A}; \quad \frac{d\alpha}{dt} = \frac{\Delta T}{A} \quad (13)$$

where  $a, A$  and  $\Delta T$  stand for the actual area, total area and ordinate of the DTA curve.

From (12) and (13) after taking the logarithms one obtains:

$$\log\left(\frac{\Delta T}{a^{1/3}}\right) = \log(A^{2/3} Z) - \frac{E}{2.303R} \cdot \frac{1}{T} \quad (14)$$

Through integration of Eq. (12) in nonisothermal conditions and keeping only two terms from the asymptotic development of the temperature integral, the following equation is obtained:

$$\log\left(\frac{a^{2/3}}{T^2}\right) = \log\left[\frac{2A^{2/3}Z}{3\beta E}\left(1 - \frac{2RT}{E}\right)\right] - \frac{E}{2.303R} \cdot \frac{1}{T} \quad (15)$$

where  $\beta$  is the heating rate.

In relationship (15) the numerical value of the expression:

$$\log\left[\frac{2A^{2/3}ZR}{3\beta E}\left(1 - \frac{2RT}{E}\right)\right]$$

varies slowly with temperature, so that it may be considered as a constant. In such conditions, relationship (15) represents a straight line equation from whose slope ( $t_g \theta = -E/2.303R$ ) the activation energy may be evaluated.

## Experimental

For the solid-solid reaction between LiCl and NaF the plots  $\log(T/a^{1/2})$  vs.  $1/T$  and  $\log(a^{2/3}/T)$  vs.  $1/T$  could be considered as straight lines for  $0.08 < \alpha < 0.47$  (Fig. 3).

In Fig. 3 both straight lines refer to sample I. The experimental points marked by ( $\cdot$ ) and ( $\times$ ) result from data processing by Eqs (14) and (15) respectively. In the case of sample II one obtains similar curves, but the slope value is greater.

The values of the activation energy depend on the presence of traces of humidity as well on mechanical treatment.

For samples I with water traces and with  $r=0.05$  cm,  $E=8.6$  kcal/mol while for samples II with dehydrated, mixed and subsequently ground reactants  $E=65$  kcal/mol.

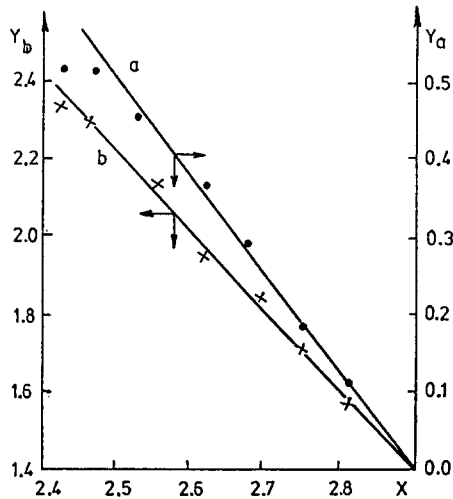


Fig. 3 Plots of Eqs (14) and (15) for the system LiCl/NaF (sample I)

$$Y_a = \log\left(\frac{\Delta T}{a^{1/3}}\right); Y_b = \log\left(\frac{a^{2/3}}{T^2}\right); X = \frac{10^3}{T}$$

The reaction has a high rate at low temperatures. This is the reason for using a Derivatograph C which allows low heating rate, and gives numerical DTA data.

The low values for the activation energy for samples I can be explained taking into account that the reaction is limited by the diffusion on the grain surface. The dehydration and mechanical activation (samples II) favour the generation of

contacts between the grains of the two reactants. In such conditions the reaction is limited by the diffusion of the ions through the crystalline lattice which determines a higher value of  $E$  and thus  $2RT/E > 1$ . Correspondingly for samples II a better linearisation of Eq. (15) was obtained.

### Conclusions

1. A model for diffusion limited solid-solid reactions was worked out;
2. As it was supposed that the diffusion fronts do not come into contact, the model is valid only for the initial period of the reaction;
3. The kinetic equation obtained satisfactorily describes the course of the reaction between LiCl(s) and NaCl(s) in nonisothermal conditions for  $0.08 < \alpha < 0.47$ ;
4. The value of the activation energy depends on the presence of water traces and on the mechanical treatment of the samples.

### References

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**Zusammenfassung** — Es wird ein Modell zur Beschreibung des einleitenden Schrittes von diffusionskontrollierten Feststoffreaktionen beschrieben. Die erhaltene kinetische Gleichung wurde zur Bestimmung der Aktivierungsenergie der Reaktion  $\text{LiCl(s)} + \text{NaF(s)} = \text{LiF(s)} + \text{NaCl(s)}$  aus DTA-Daten angewendet.