

DIFFUSION AND REACTION STUDIES IN INORGANIC SOLID-SOLID SYSTEM

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Diffusion and reaction between two inorganic solids, zinc oxide and aluminium oxide, was undertaken in single cylindrical pellets with their end faces in contact with each other. Assuming a second-order irreversible reaction between the reactants, the second-order rate constants were determined as functions of particle size, compaction pressure and temperature. The activation energies required for reaction alone were computed. Generalized correlations for the second-order rate constant as a function of initial porosity of the compact were also established.

Introduction

Solid-state reactions, particularly in the formation of complex metallic oxides, carbonates and silicates at high temperatures, are of considerable industrial importance. Yet there are very few studies in the literature giving information about kinetics and diffusion in solid systems. One of the reasons is the intricate relationship between the diffusion and reaction processes. Hence it is evident that more experimental and theoretical work are needed to obtain quantitative information regarding the isolation of diffusion and reaction in solid systems.

To obtain information on diffusion and reaction in solids, the programme of experimental work is divided into three parts:

- i) To measure the combined diffusion and reaction resistances in mixed powders (reactants in well-mixed state);
- ii) to measure the diffusivities of each of the reactants in the product;
- iii) to measure the diffusion and reaction resistances in single cylindrical pellets.

The present study corresponds to the third step, while the first and second steps are dealt with separately.^{1,2)}

Each of the parts above has particular significance.

The information on mixed powders is of more practical or utilitarian value than of fundamental value. For example, all commercial ferrites are manufactured from mixed powders. Hence the data help to establish optimum conditions of processing treatments. The data on powders apply only to particular

systems used in the experiments. As reaction proceeds, contact area changes in a very complex manner. The increase in contact area with time cannot be measured experimentally, even in the case of spherical particles. The geometry becomes three-dimensional and complex. Hence it is almost impossible to deduce the rate-determining step in mixed powder systems. Data of this type are therefore of limited value, from the fundamental viewpoint.³⁾

On the other hand, if the aim is to determine the rate-controlling step, the experimental conditions should be so chosen that the reaction is confined to an interface of a relatively simple geometry. The area of interface should not change as reaction proceeds.

The present experimental work using bulk materials in the form of single cylindrical pellets conforms to these conditions of simple geometry and no change in area of the interface during the reaction. The diffusivities of each of the reactants into the product layer were measured under the conditions of the same geometry. The objective of isolating diffusion and reaction resistances from the combined diffusion and reaction data and the diffusion data is made possible.

Experimental data with porous and non-porous specimens separately give useful information about the effect of controlling factors such as porosity on diffusion and reaction.

The activation energies for reaction alone are determined and compared with those of diffusion. This procedure gives definite conclusions regarding the rate-determining step.

Very few studies are available on interdiffusion associated with reaction in the literature. They are

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presented briefly here. The following studies do not give any information on the measurement of diffusivities under similar geometrical conditions. Hence no information on delineation of diffusion and kinetics has been brought out in these studies.

Rigby and Cutler⁴⁾ reported the enthalpy of activation for diffusion and reaction between Fe_xO – MgO as $47.5 \text{ kcal} \cdot \text{mol}^{-1}$. The activation energy was independent of vacancy concentration.

Grescovich and Stubican⁵⁾ studied the solid-state reaction between MgO and Cr_2O_3 and found that interdiffusion associated with reaction was dependent upon concentration and increased linearly up to 1873 K with increasing mole fractions of vacancies.

Jones and Cutler⁶⁾ observed the counter-diffusion of Mg and Mn ions through a rigid oxygen lattice in the case of solid-state reaction between MnX and MgO . The reaction temperatures were 1653 K in air and 1773 K in an oxygen atmosphere at a pressure of $9.81 \times 10^{-5} \text{ Nm}^{-2}$ atmospheres. The activation energy was $41 \text{ kcal} \cdot \text{mol}^{-1}$.

Br. Marvin Appel and Park⁷⁾ reported chemical interdiffusion in the case of NiO – CaO system at 1623 K and 1800 K. The diffusivities increased exponentially with increasing Ni concentration.

Arrowsmith and Smith⁸⁾ developed equations showing the effects of diffusion and reaction rate constant on the concentration profiles for combined diffusion and reaction for single cylindrical pellets of reactants with their end faces in contact.

Studies on diffusion and reaction in the case of low-temperature organic reaction between phthalic anhydride and paranitraniline using single cylindrical pellets were reported by Ramachandran *et al.*⁹⁾ Activation energies for diffusion and reaction were obtained separately. It was found that activation energy for diffusion was higher.

Tamhankar and Patwardhan¹⁰⁾ presented the mathematics of unsteady-state diffusion and reaction in a solid–solid system by resorting to nonlinear regression analysis to delineate the rate constant and diffusivity.

In the literature no mathematical models are developed for diffusion coupled with reaction for high-temperature inorganic solid–solid systems.

The present work reports diffusion and reaction studies in the case of an inorganic solid–solid system, zinc oxide and aluminium oxide, using single cylindrical pellets.

1. Experimental

The experimental method was similar to that described elsewhere²⁾ except that two cylindrical rods of zinc oxide and aluminium oxide were kept with their end faces in contact with each other. The analysis was done with an electron probe micro analyser. Check

was made for the movement of a wire marker and product formation at the interface. From the above tests and from the concentration profiles obtained, it was found that only zinc oxide diffused, with no counter-diffusion of aluminium oxide, indicating zinc aluminate formation only on the side of the aluminium oxide. The observations in this section confirmed further the experimental observations made earlier.²⁾

Based on the experimental results above, simultaneous one-dimensional axial diffusion and second-order reaction are chosen to characterise the governing partial differential equations of the system to determine the basic diffusional and kinetic parameters.

2. Experimental Result and Discussion

The experimental runs for diffusion and reaction in single cylindrical pellets were conducted at various experimental conditions. The scope of the experimental work was identical to that for diffusion studies in single cylindrical pellets described earlier.²⁾ Each run consisted of two cylindrical composite pellets containing zinc oxide and aluminium oxide treated identically to check the reproducibility.

2.1 Theory

Based on the experimental observations, the following mathematical model was developed.

The mass balances for the two components A and B were

$$\frac{\partial a}{\partial t} = D_o \frac{\partial}{\partial x} \left(e^{a^\alpha} \frac{\partial a}{\partial x} \right) - kab \quad (1)$$

and

$$\frac{\partial b}{\partial t} = -kab \quad (2)$$

The initial conditions for the system were

$$a = a_0, \quad b = c = 0 \quad \text{for } x < 0 \quad (3)$$

$$a = c = 0, \quad b = b_0 \quad \text{for } x > 0 \quad (4)$$

For long rods, concentration changes will not occur at the outer ends. For this system the boundary conditions were

$$a = a_0, \quad b = c = 0 \quad \text{at } x = -\infty \quad (5)$$

$$a = c = 0, \quad b = b_0 \quad \text{at } x = +\infty \quad (6)$$

The following dimensionless variables were defined:

$$\xi = x \left(\frac{a_0 k}{D_o} \right)^{1/2} \quad (7)$$

$$\tau = a_0 k t \quad (8)$$

$$\alpha = a/a_0 \quad (9)$$

$$\beta = b/b_0 \quad (10)$$

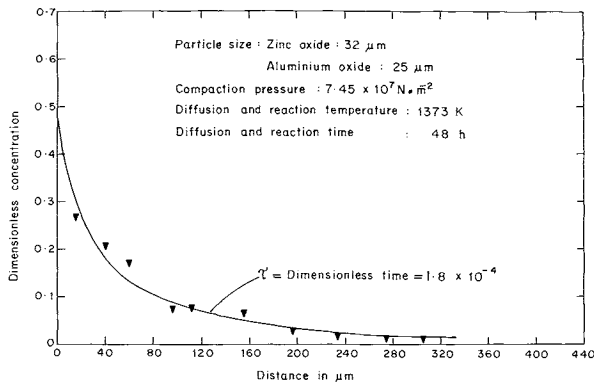


Fig. 1. Comparison of theoretical and experimental concentration dimensionless profiles ($\alpha = a/a_0$ vs. x) for 48 h for diffusional and reaction studies in single cylindrical pellets for compaction pressure of $7.45 \times 10^7 \text{ Nm}^{-2}$.

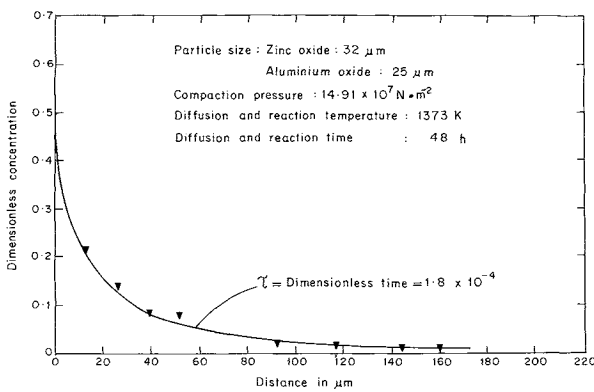


Fig. 2. Comparison of theoretical and experimental dimensionless profiles ($\alpha = a/a_0$ vs. x) for 48 h for diffusion and reaction studies in single cylindrical pellets for compaction pressure of $14.91 \times 10^7 \text{ Nm}^{-2}$.

The final expressions in terms of the dimensionless variables were

$$\frac{\partial \alpha}{\partial \tau} = \frac{\partial}{\partial \xi} \left((e^{a'\alpha}) \frac{\partial \alpha}{\partial \xi} \right) - \alpha \beta \quad (11)$$

$$\frac{\partial \beta}{\partial \tau} = -\alpha \beta \quad (12)$$

Equations (11) and (12) with the initial and boundary conditions represented by Eqs. (3), (4), (5) and (6) and considering that $a_0 = b_0$ are first written in three-point finite difference form. The equations were then solved numerically using IBM 360/44 for a and b as function of ξ , τ and a' .

2.2 Procedure for the calculation of k

The experimental dimensionless profiles for differential experimental conditions were then matched with various theoretical concentration (dimensionless) profiles. This is shown in **Figs. 1** and **2** for extreme experimental conditions. The matching was done in a manner that resulted in minimum average deviation between the theoretical and experimental dimensionless concentration profiles.

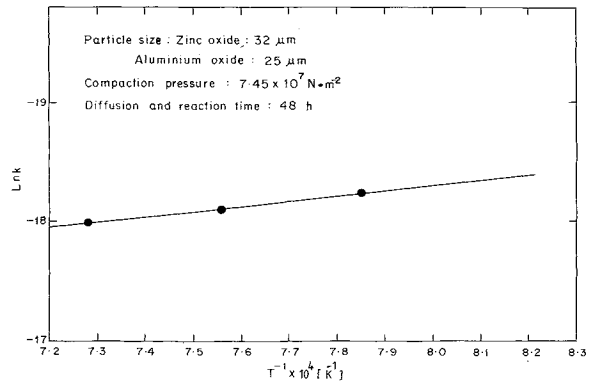


Fig. 3. Arrhenius plot for diffusion and reaction studies in single cylindrical pellets for compaction pressure of $7.45 \times 10^7 \text{ Nm}^{-2}$.

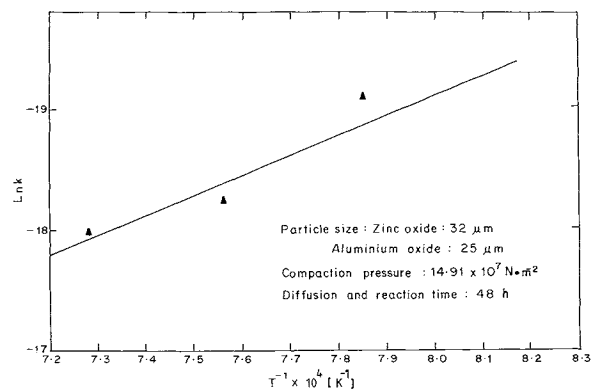


Fig. 4. Arrhenius plot for diffusion and reaction studies in single cylindrical pellets for compaction pressure of $14.91 \times 10^7 \text{ Nm}^{-2}$.

Values of second-order reaction rate constant, k , were established as functions of temperature at various experimental conditions.

3. Discussion of Results

Arrhenius-type correlations were established and are shown in **Figs. 3** and **4** for extreme experimental conditions. From these plots the activation energies and second-order rate constants for reaction alone were calculated and are given in **Table 1**.

3.1 Generalised correlations

The following generalised correlations were obtained to represent the effect of initial porosity of compact ϵ_0 on reaction rate constant:

$$\ln k = (177.47 - 2.79\epsilon_0) - \left(\frac{525.5 - 7.5\epsilon_0}{RT} \right) \quad (13)$$

The following shows the agreement between predicted and experimental values.

	Average deviation
Activation energy, E	+14.9%
Frequency factor, k_0	-23.4%
Reaction rate constant, k	+8.8%

Table 1. Arrhenius-type correlations for the reaction rate constants for diffusion and reaction studies in single cylindrical pellets

	Particle size [μm]	Compaction pressure [$\text{N}\cdot\text{m}^{-2}$]	Percentage initial porosity [ϵ_0]	Correlation
1.	ZnO: 32	7.45×10^7	69.5	$k = 1.7 \times 10^{-7} \times \exp(-6.6/RT)$
2.	Al_2O_3 : 25	11.18×10^7	68.1	$k = 1.182 \times 10^{-6} \times \exp(-12/RT)$
3.		14.91×10^7	65.7	$k = 3.061 \times 10^{-3} \times \exp(-33/RT)$

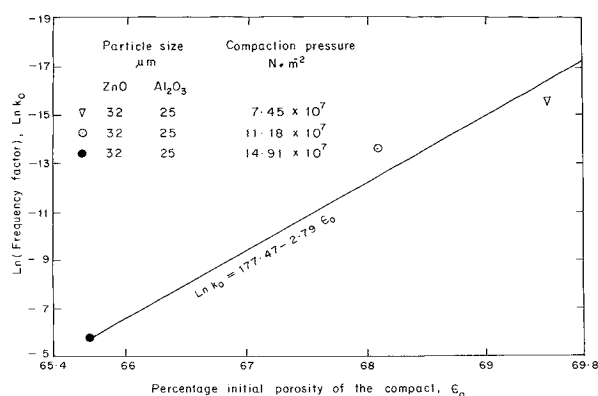


Fig. 5. Correlation plot of frequency factor with initial porosity of the compact for diffusion and reaction studies in single cylindrical pellets.

The constants in Eq. (13) were characteristic of the solid system involved. The correlation plots are shown in Figs. 5 and 6.

The variation in the final porosity of compacts was less than 2%, and thus was not taken into consideration in the generalised correlations.

4. Conclusion

From experiments with single cylindrical pellets, it was found that the values of second-order rate constant k were of the order of $10^{-8} \text{ cm}^{-3} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$. The activation energies for the reaction alone were calculated. Generalised correlations for reaction rate as a function of initial porosity of compact, ϵ_0 , were also established. Thus the objective of delineating between mass transfer and kinetics resistance from diffusion and diffusion and reaction data was achieved.

Nomenclature

a	= concentration of A	[$\text{mol}\cdot\text{cm}^{-3}$]
a'	= constant relating temperature- and concentration-dependent average diffusivity with fundamental diffusivity (temperature-dependent and concentration-independent) and a in Eq. (1)	
a_0	= concentration of pure A	[$\text{mol}\cdot\text{cm}^{-3}$]

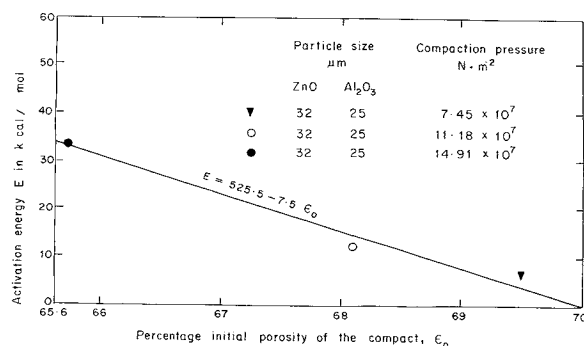


Fig. 6. Correlation plot of activation energy with initial porosity of the compact for diffusion and reaction studies in single cylindrical pellets.

b	= concentration of B	[$\text{mol}\cdot\text{cm}^{-3}$]
b_0	= concentration of pure B	[$\text{mol}\cdot\text{cm}^{-3}$]
c	= concentration of C	[$\text{mol}\cdot\text{cm}^{-3}$]
E	= Arrhenius activation energy based on k	[$\text{kcal}\cdot\text{mol}^{-1}$]
k	= reaction rate constant	[$\text{cm}^3\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$]
k_0	= frequency factor for Arrhenius correlation for diffusion and reaction in single cylindrical pellets	[$\text{cm}^3\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$]
R	= gas constant	
r	= reaction rate	[$\text{mol}\cdot\text{cm}^{-3}\cdot\text{s}^{-1}$]
T	= absolute temperature	[K]
t	= time	[s]
x	= axial distance in cylindrical pellet measured from original function of dissimilar pellets	[cm]
α	= dimensionless concentration of A, a/a_0 in Eq. (9)	
β	= dimensionless concentration of B, b/b_0 in Eq. (10)	
ϵ_0	= initial porosity of the compact	
ζ	= dimensionless distance, $X(a_0k/D_0)^{1/2}$ in Eq. (7)	
τ	= dimensionless time, a_0kt in Eq. (8)	
μm	= micrometer or micron	

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