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DIFFUSION STUDIES IN INORGANIC SOLID-SOLID SYSTEM

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Diffusivity measurements between two inorganic solids, zinc oxide and zinc aluminate, in the absence of reaction was undertaken with particle size, compaction pressure, diffusion temperature and diffusion time as variables. The present work was mainly concerned with the experimental techniques of measurement and the establishment of the concentration profile for diffusion of zinc oxide into the zinc aluminate through which fundamental as well as concentration and temperature diffusivities were determined. Activation energies required for fundamental as well as concentration and temperature diffusion were calculated and reported. Generalized correlations were also established.

Introduction

Zinc aluminate is formed between the reactants zinc oxide and aluminum oxide by solid-state reaction. Diffusion of each of the reactants is essential for the solid-state reaction to proceed. It is in this context that information on diffusivities and their measurement are considered necessary.

The mechanism of diffusion in solid-solid systems can be classified into three categories:

(1) Volume or bulk diffusion within the individual particles;

(2) boundary diffusion at particle-particle interface, or along the grain boundaries in polycrystalline substances, or at the interface between two dissimilar pellets; and

(3) pore surface diffusion along the surface of the particles.

An attempt is made in the present study to indicate the factors governing the relative importance of various mechanisms of diffusion.

The experimental study in this part refers to the

measurement of diffusivities in single cylindrical pellets when the pellets of either of the reactants and product are kept with their end faces in contact with each other. This procedure is chosen so as to avoid the consideration of change in the interfacial area. In this way, it is felt easier to correlate the experimental data by a suitable theory and to make successful predictions.

Very few studies are available in the literature regarding diffusion mechanisms in solid-solid systems.¹⁻⁵⁾ The work on inorganic systems mainly consists of studies on oxides and ionic crystals.^{2,6-22)}

Among the diffusion studies in organic systems, one recently reported was on the diffusion of phthalic anhydride in a phthalyl derivative of sulphathiazole by Arrowsmith and Smith.²³⁾ They report pore surface diffusion.

The present studies on diffusion are confined to the regular geometry of the interfacial area based on single cylindrical pellets. Each of the reactant pellets is kept in contact with pellets of product. Diffusivities are obtained as functions of particle size, compaction pressures, diffusion temperature and concentration of

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the diffusing component in the pellet.

1. Experimental

1.1 Preparation of pure product sample

Aluminum oxide and zinc oxide powders were mixed in the molar proportion of one to five respectively. Solid-state reaction was carried out at a temperature of 1373 K and for a reaction time of 48 hr. All of the aluminum oxide was reacted to zinc aluminate. The unreacted zinc oxide taken in excess was removed from the solid reaction products mixture by leaching out with dilute hydrochloric acid. The final solid substance left was the inert product (zinc aluminate).

1.2 Diffusivity measurements

A weighed sample of the product—zinc aluminate—of a particular particle size was placed in the mould and a certain compaction pressure was applied by means of the plunger in the laboratory hydraulic pellet press. Then a platinum wire marker of 0.00014 m diameter and 0.008 m length was placed over the pellet. Over the wire marker, a weighed sample of zinc oxide or aluminum oxide of the desired particle size was placed and the same compaction pressure was applied. Then the composite pellet was taken out of the mould, placed in a silica crucible and subjected to diffusion temperature for a certain time. The composite pellet was then cooled to room temperature. Reactant and product pellets were separated at the interface. A check for the movement of the wire marker was made. The individual pellets were then subjected to quantitative analysis by an electron probe micro-analyser for the diffusion of zinc ions. The porosities of pellets before and after diffusion experiments were measured.

2. Experimental Results and Discussion

2.1 Observations

The diffusion runs were conducted with composite pellets of zinc oxide–zinc aluminate and aluminum oxide–zinc aluminate, separately, at various experimental conditions and the scope of experimental data is given in **Table 1**. Each set of experimental runs consisted of 2 or 3 composite pellets treated identically. This allowed the reproducibility of the data to be checked. The following observations were made during the experiments.

(i) There was no movement of the wire marker from the interface, suggesting the absence of bulk diffusion. In other words, movement of substance due to a pressure gradient was non-existent.

(ii) Electron probe analysis gave a profile only on the side of zinc aluminate in the case of experiments with the composite pellet, zinc oxide–zinc aluminate. There were no concentration changes on the side of zinc oxide. This suggested that counter-diffusion of

Table 1. Scope of experimental data for diffusion studies in single cylindrical pellets

1. Particle size	ZnO: 32 μm ZnAl ₂ O ₄ : 25 μm
2. Compaction pressure	7.45 $\times 10^7 \text{ Nm}^{-2}$ 11.18 $\times 10^7 \text{ Nm}^{-2}$ 14.91 $\times 10^7 \text{ Nm}^{-2}$
3. Diffusion temperature	1273 K 1323 K 1373 K
4. Diffusion time	48 h

zinc aluminate was absent. No diffusion was observed on either side in the case of experiments with aluminum oxide–zinc aluminate composite pellet.

(iii) The concentration gradients of zinc on the side of zinc aluminate increased with the increase in initial porosity of the compacts and diffusion temperature.

(iv) Scanning of the zinc aluminate pellet was done with the electron probe in a direction perpendicular to the axis of the composite pellet, to identify any existing radical diffusion. The results proved that radical diffusion was completely absent.

3. Theory

Based on the experimental observations the following mathematical model for one-dimensional axial diffusion in a binary system was developed:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial X} \left(D_{Loc} \frac{\partial C}{\partial X} \right) \quad (1)$$

Where,

$$D_{Loc} = D_o e^{a\alpha} \quad (2)$$

The following dimensionless variables were defined:

$$\tau = \frac{D_o t}{R^2} \quad (3)$$

$$\alpha = \frac{C}{C_o} \quad (4)$$

$$\xi = \frac{X}{R} \quad (5)$$

In terms of the dimensionless variables, Eq. (1) was written as:

$$\frac{\partial \alpha}{\partial \tau} = e^{a\alpha} \left(\frac{\partial^2 \alpha}{\partial \xi^2} \right) + a e^{a\alpha} \left(\frac{\partial \alpha}{\partial \xi} \right)^2 \quad (6)$$

Equation (6) is a second-order, non-linear partial differential equation for which analytical solution is not available. Hence, this equation was first written in the three-point finite difference form and then solved numerically using an IBM 360/44.

The finite difference form of Eq. (6) is

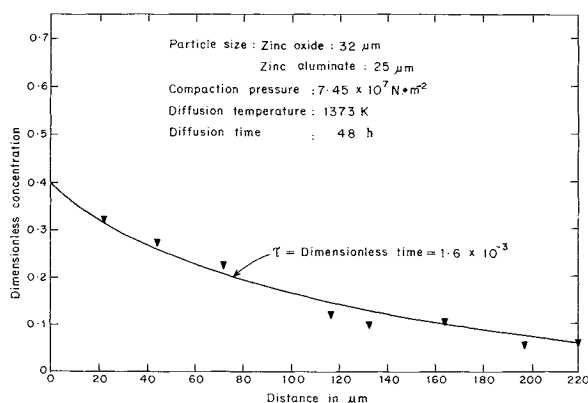


Fig. 1. Comparison of theoretical and experimental dimensionless concentration profile ($\alpha = C/C_0$ vs. X) for diffusion studies in single cylindrical pellets. —, theoretical; ▼, experimental.

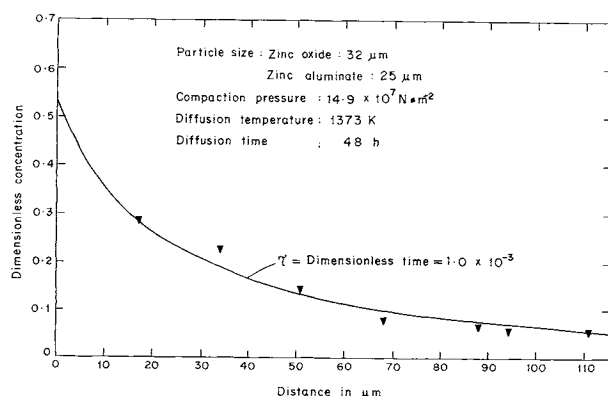


Fig. 2. Comparison of theoretical and experimental dimensionless concentration profiles ($\alpha = C/C_0$ vs. X) for 48 h for diffusion studies in single cylindrical pellets. —, theoretical; ▼, experimental.

$$\alpha_{i,j+1} = \alpha_{i,j} + 0.25e^{a\alpha} [-(\alpha_{i+1,j}^{-2} \alpha_{i,j} + \alpha_{i-1,j}) + a(\alpha_{i+1,j} - \alpha_{i,j})^2] \quad (7)$$

Where i is the space coordinate index and j is the time coordinate index. $i=0$ represents the interface with the initial conditions.

$$\alpha_{1,0} = 0.0 \quad (8)$$

$$\alpha_{0,0} = 0.5 \quad (9)$$

$$\alpha_{-1,0} = 1.0 \quad (10)$$

The dimensionless concentration profiles (α vs. ξ) were developed as functions of C and a . The experimental dimensionless concentration profiles were then matched with theoretical ones, to obtain the most appropriate temperature-dependent and concentration-independent fundamental diffusivity, D_o . A comparison of the experimental and theoretical concentration profiles is shown in Figs. 1 and 2. The average deviation between theoretical and experimen-

tal values of dimensionless concentration profiles was less than $\pm 12\%$ for most appropriate values of D_o for various experimental conditions. The magnitude of diffusivities was in conformity with those reported by Poch²⁴) for diffusion of zinc in α -alumina.

The D_{Loc} values were calculated as functions of a and α as given by Eq. (2) for various experimental conditions and \bar{D} was obtained as averaged over the entire concentration profile. This was then correlated as functions of ϵ_o and T as in Eq. (11).

4. Discussion of Results

The values of diffusivity obtained as described above increased with increasing temperature and particle size and decreasing compaction pressure. This suggested the importance of pore surface diffusion in the present system. Activation energies were calculated and are presented in Tables 2 and 3 for average and fundamental diffusion. The Arrhenius-type correlations are presented in Tables 4 and 5 and in Figs. 3 and 4.

The following correlation relating diffusivity (averaged over concentration profile) to temperature and initial porosity of the compact was obtained.

$$\ln \bar{D} = (34.2 - 0.73\epsilon_o) - \left(\frac{174 - 2.44\epsilon_o}{R_g T} \right) \quad (11)$$

The following shows the agreement between predicted and experimental values:

	Average deviation
Activation energy, E	+0.2%
Diffusion frequency factor, \bar{D}_o	+0.5%
Diffusivity, \bar{D}	-1.6%

The constants in Eq. (11) are characteristics of the solid system involved. The correlation plots are shown in Figs. 5 and 6. Another correlating equation relating D_o , which is the fundamental diffusivity, independent of concentration effects, to ϵ_o and temperature was obtained as follows:

$$D_o = \exp(59.5 - 1.30\epsilon_o) \exp\left(\frac{3.75\epsilon_o - 228}{R_g T}\right) \quad (12)$$

The following shows the agreement between predicted and experimental values:

	Average deviation
Activation energy, E_o	+0.6%
Frequency factor, D_{oo}	+20.9%
Fundamental diffusivity, D_o	+17.6%

a was correlated to ϵ_o and T by the following equation

$$a = \left(\frac{4.217 \times 10^5 - 9.49\epsilon_o}{T} \right) + (7.69\epsilon_o - 352) \quad (13)$$

The relation between Eqs. (2) and (13) results in Eq. (14)

Table 2. Activation energies for diffusion (based on temperature- and concentration-dependent average diffusivities) in diffusion studies in single cylindrical pellets

Particle size [μm]	Compaction Pressure [Nm^{-2}]	Percentage initial porosity [ϵ_0]	Diffusion time [h]	Activation energy [$\text{kcal}\cdot\text{mol}^{-1}$]
1. ZnO: 32 ZnAl ₂ O ₄ : 25	7.45×10^7	52.2	48	46.4
2. ZnO: 32 ZnAl ₂ O ₄ : 25	11.18×10^7	50.4	48	51.1
3. ZnO: 32 ZnAl ₂ O ₄ : 25	14.91×10^7	46.2	48	61.1

Table 3. Activation energies for fundamental diffusion (based on temperature-dependent and concentration-independent diffusivities) in diffusion studies in single cylindrical pellets

Particle size [μm]	Compaction Pressure [Nm^{-2}]	Percentage initial porosity [ϵ_0]	Diffusion time [h]	Activation energy [$\text{kcal}\cdot\text{mol}^{-1}$]
1. ZnO: 32 ZnAl ₂ O ₄ : 25	7.45×10^7	52.2	48	32.8
2. ZnO: 32 ZnAl ₂ O ₄ : 25	11.18×10^7	50.4	48	37.4
3. ZnO: 32 ZnAl ₂ O ₄ : 25	14.91×10^7	46.2	48	55.3

Table 4. Arrhenius-type correlations for diffusion (based on temperature- and concentration-dependent average diffusivities) in diffusion studies in single cylindrical pellets

Particle size [μm]	Compaction Pressure [Nm^{-2}]	Percentage initial porosity [ϵ_0]	Correlation
1. ZnO: 32 ZnAl ₂ O ₄ : 25	7.45×10^7	52.2	$\bar{D} = 1.797 \times 10^{-2} \times \exp(-46.4/RT)$
2. ZnO: 32 ZnAl ₂ O ₄ : 25	11.18×10^7	50.4	$\bar{D} = 6.591 \times 10^{-2} \times \exp(-51.09/RT)$
3. ZnO: 32 ZnAl ₂ O ₄ : 25	14.91×10^7	46.2	$\bar{D} = 1.822 \times \exp(-61.1/RT)$

Table 5. Arrhenius-type correlations for fundamental diffusion based on temperature-dependent and concentration-independent diffusivities in diffusion studies in single cylindrical pellets

Particle size [μm]	Compaction Pressure [Nm^{-2}]	Percentage initial porosity [ϵ_0]	Correlation
1. ZnO: 32 ZnAl ₂ O ₄ : 25	7.45×10^7	52.2	$\bar{D}_0 = 2.332 \times 10^{-4} \times \exp(-32.8/RT)$
2. ZnO: 32 ZnAl ₂ O ₄ : 25	11.18×10^7	50.4	$\bar{D}_0 = 9.654 \times 10^{-4} \times \exp(-37.4/RT)$
3. ZnO: 32 ZnAl ₂ O ₄ : 25	14.91×10^7	46.2	$\bar{D}_0 = 5.601 \times 10^{-1} \times \exp(-55.3/RT)$

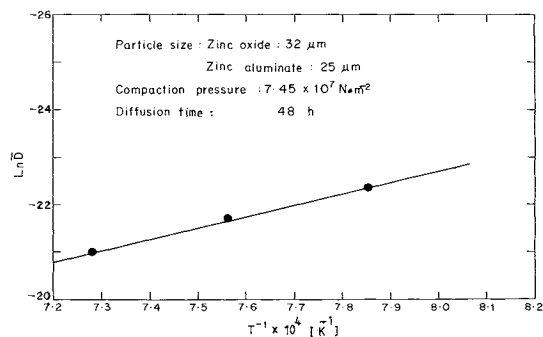


Fig. 3. Arrhenius plot for diffusion studies in single cylindrical pellets.

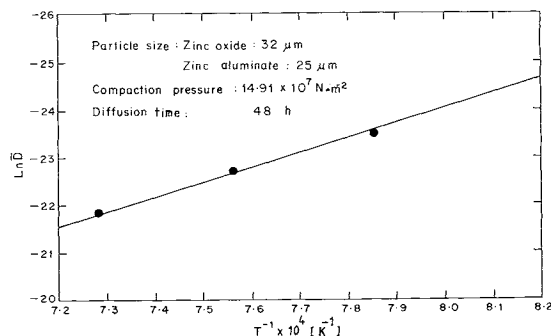


Fig. 4. Arrhenius plot for diffusion studies in single cylindrical pellets.

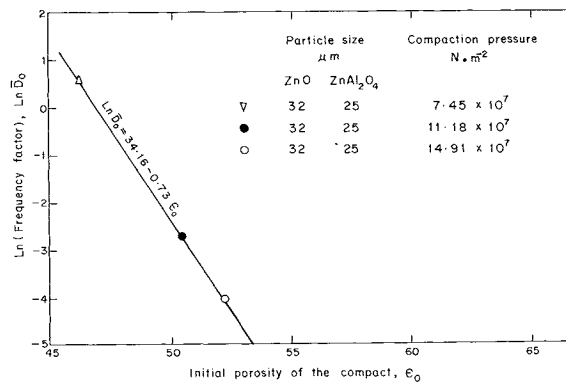


Fig. 5. Correlation of frequency factor (based on temperature- and concentration-dependent average diffusivities \bar{D}) for diffusion studies in single cylindrical pellets.

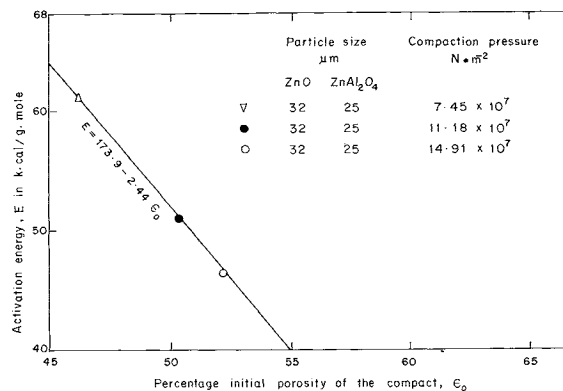


Fig. 6. Correlation of activation energy (based on temperature- and concentration-dependent average diffusivities \bar{D}) for diffusion studies in single cylindrical pellets.

$$D_{Loc} = \exp(59.5 - 1.36\varepsilon_o) \exp\left(\frac{3.75\varepsilon_o - 228}{R_g T}\right) \times \exp\left(\frac{4.217 \times 10^5 - 9.49\varepsilon_o}{T}\right) + (7.69\varepsilon_o - 352) \quad (14)$$

The variation in the final porosity of the compacts was experimentally found to be less than 2%, and thus was not taken into consideration in the generalized correlations.

5. Conclusion

Increase in particle size and decrease in compaction pressure resulted in a cumulative effect of increase in initial porosity of the compacts. The values of \bar{D} increased with increase in initial porosity of the compacts. The present work provided quantitative proof for the pore surface diffusion being predominant in single cylindrical pellets, through the generalized correlations. Also, the absence of marker movement proved the insignificance of bulk or volume diffusion through a pressure gradient.

The discontinuity in concentration profiles at the interface of dissimilar pellets indicated the resistance being offered due to boundary diffusion.

Nomenclature

a	= constant relating D_{Loc} , D_o and α in Eq. (2)
C	= concentration of A at any distance X , from the interface, at time t , for diffusion [mol·cm ⁻³]
C_o	= concentration of pure A [mol·cm ⁻³]
D_{Loc}	= temperature- and concentration-dependent local diffusivity [cm ² ·s ⁻¹]
\bar{D}	= temperature- and concentration-dependent average diffusivity [cm ² ·s ⁻¹]
\bar{D}_o	= frequency factor in Arrhenius correlation for diffusion involving \bar{D} [cm ² ·s ⁻¹]
D_o	= fundamental diffusivity (temperature-dependent and concentration-independent) [cm ² ·s ⁻¹]
D_{oo}	= frequency factor based on fundamental diffusivity [cm ² ·s ⁻¹]
E	= Arrhenius activation energy based on \bar{D} [kcal·mol ⁻¹]
E_o	= Arrhenius activation based on fundamental diffusivity D_o [kcal·mol ⁻¹]
R	= radius of cylindrical pellets [cm]
R_g	= gas constant [kcal·mol ⁻¹ ·K ⁻¹]
T	= absolute temperature [K]
t	= time [s]
X	= axial distance in cylindrical pellet measured from original junction of dissimilar pellets [cm]

α	= dimensionless concentration of A or zinc, C/C_o in Eq. (3)
ε_o	= percentage initial porosity of the compact
ξ	= dimensionless distance, X/R in Eq. (5)
τ	= dimensionless time, $D_o t/R^2$ in Eq. (3)
μm	= micrometer or micron

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