R & D NOTES

Analysis of Gas-Solid Reactions with Zero-Order Dependency on Gas and Solid: Concept of Jumping Reaction Zones

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INTRODUCTION

Gas-solid noncatalytic reactions have generally been modeled assuming the reaction to be first order with respect to the gaseous reactant. The order with respect to the solid reactant has been ascribed various values from zero to unity. For example, Ishida and Wen (1968) and Mantri et al. (1976) have assumed a zero-order dependence of the rate on the solid concentration. Recently models based on nonlinear rate forms for the gas-phasee reactant have beeen developed. For example, Dudukovic and Lamba (1978) developed the zone model assuming the reaction to be zero order with respect to the gas and first order with respect to solid. An interesting problem arises for the situation where the reaction is intrinsically zero order with respect to both gas and solid (zero-zero-order reaction). This does not appear to have been analyzed in any reported study so far. Such a case is of considerable theoretical interest and may also be of practical importance in some situations since the model presented here provides a convenient mathematical representation of systems which closely approximate zero-zero kinetics.

The analysis of the problem is simple for the situation where no diffusional gradients exist. For systems with significant diffusional gradients the reaction zone gets frozen at a position near the interface till the solid hereagets completely converted. The reaction zone then jumps to an adjacent position and remains there again till the solid in the new zone is completed exhausted. Thus we obtain a new class of models for this situation which may be called as the jumping zone model.

The purpose of this note is to present a theoretical analysis of a gas-solid reaction which is zero order with respect to both components. A criterion is developed to predict the conditions for no significant diffusional gradients for this case. The analysis is extended to the case when these gradients are significant. Procedures for prediction of the number of jumping zones which can develop and for conversion-time behaviour of the system are presented.

CRITERION FOR NO DIFFUSIONAL GRADIENTS

The criterion for no diffusional gradients for $a(0, 0)$ order reaction can be easily formulated following the earlier work on catalytic zero-order reactions (for example, Wheeler, 1951; Lin and Lih, 1971; Krishna and Ramachandran, 1976). Physically the concentration of gas, A, should be a finite positive quantity at the centre of the catalyst and this is satisfied if the following condition is satisfied.

$$\phi_0\left[1+\frac{2}{Bi}\right]^{1/2} \leqslant \sqrt{6} \qquad (1)$$

where ϕ_o is the Thiele modulus for the zero-zero-order reaction and is defined as $(k_oR^2/D_eA_g)^{1/2}$ and Bi is the Biot number for external mass transfer.

When criterion is satisfied the reaction will occur at a uniform rate throughout the pellet and no distinct reaction zone will be observed in the pellet. The conversion-time relationship for this case is given as:

$$x = \theta \qquad (2)$$

where θ is the dimensionless time determined as $\gamma k_o\, t/B_o$

ANALYSIS OF THE JUMPING ZONE CASE

When criterion is not satisfied the reaction will occur initially in a zone close to the surface. Once this zone is completely reacted the reaction zone will jump to an adjacent region. This process will continue until the pellet is completely consumed. The thickness of the zone corresponds to the depth of penetration of the reactant gas into the pellet. In the following section we present the analysis for this case.

Consider the reaction zone to be located between the positions λ_2 and λ_1, in the pellet as shown in the Figure 1. The concentration at position λ_1 (a_{λ_1}) can be shown to be equal to the following equation by considering the rate of mass transfer through the gas film and the product layer enclosed in the region λ_1 to 1

$$1 - a_{\lambda_1} = J\left[1 + \frac{Bi(1-\lambda_1)}{\lambda_1}\right] \qquad (3)$$

where J represents the dimensionless flux of A into the pellet defined as $R_A/(4\pi R^2 k_g A_g)$.

The diffusion equation for the region λ_2 to λ_1 is

$$\nabla^2 a = \phi_0^2 \qquad (4)$$

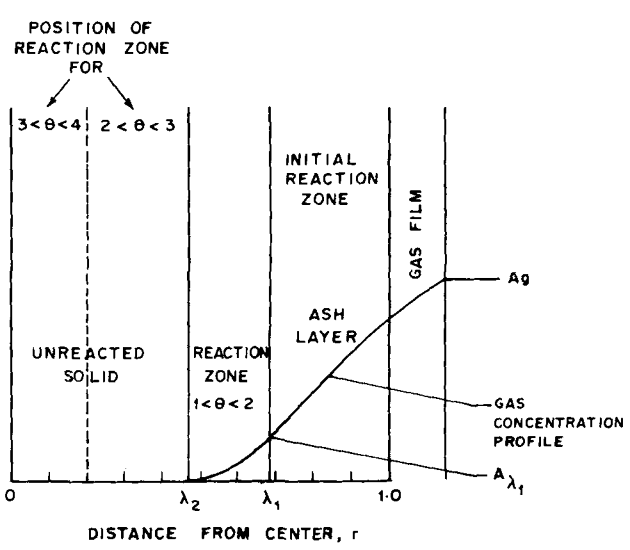

Figure 1. Position of reaction zone for $1 < \theta < 2$; for $\phi_o = 4$, $Bi = 10$.

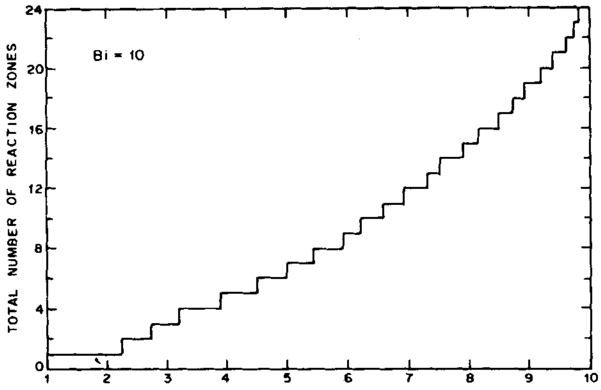

Figure 2. Number of reaction zones which develop in the pellet for various values of ϕ_o.

with the boundary conditions at

$$r = \lambda_1 \quad a = a_{\lambda_1} \tag{5}$$

$$r = \lambda_2 \quad a = 0, \frac{da}{dr} = 0 \tag{6}$$

Also the quantity J is related to the flux of A at λ_1 as

$$J = \frac{\lambda_1^2}{Bi}\left(\frac{da}{dr}\right)_{\lambda_1} \tag{7}$$

Solving the above set of equations and eliminating the unknown terms a_{λ_1} and J, we obtain the following implicit cubic equation for λ_2:

$$\lambda_2^3\left[\frac{\phi_0^2}{3Bi}\left(1 + Bi\,\frac{(1-\lambda_1)}{\lambda_1}\right) - \frac{\phi_0^2}{3\lambda_1}\right] + \frac{\phi_0^2\lambda_2^2}{2} + 1 - \frac{\phi_0^2\lambda_1^2}{6} - \frac{\phi_0^2\lambda_1^3}{3Bi}\left[1 + Bi\,\frac{(1-\lambda_1)}{\lambda_1}\right] = 0 \tag{8}$$

At time zero, $\lambda_1 = 1$ and the zone will be located between λ_2 and 1 where λ_2 is the solution of the above equation with $\lambda_1 = 1$. The zone will remain fixed here till complete reaction takes place and this will occur in a dimensionless time equal to unity. Then a second zone will be formed the thickness of which can be calculated in the same manner. The dimensionless time required for complete conversion of the pellet can be shown to be equal to the number of zones which develop in the pellet as time progresses.

The number of zones which can develop is shown in Figure 2 as a function of ϕ_o for $Bi = 10$. It is seen that the number of zones which develop increases significantly as the Thiele modulus increases. For $\phi_o = 10$ as many as twenty four zones can develop and here the process may appear to proceed in a topochemical manner. An illustrative $x - \theta$ plot is shown in Figure 3 for a particular case of $Bi = 10$ for three values of ϕ_o.

At higher values of ϕ_o the model predictions approach those of the sharp interface model with a rapid reaction. (The predictions of a sharp interface model for $\phi_o = 6$ are shown as dotted line in Figure 3.) This is consistent with the fact that the number of zones increases significantly as the Thiele modulus increases. Thus the *sensitivity* of the conversion–time curves to the type of model assumed is highest for low ranges of Thiele modulus and any possible model verification must be attempted in this range. Also, the model will be mainly applicable to strongly adsorbing gaseous reactants. For such systems the dissection and examination of the pellets at various stages of reaction may be of interest for proper choice of the model.

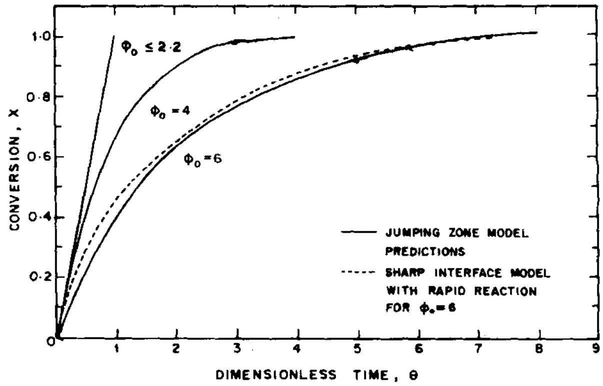

Figure 3. Conversion-time behavior for a zero-zero-order reaction, $Bi = 10$.

NOTATION

a = dimensionless concentration of gas A
A_g = concentration of gas in the external fluid
B_o = initial concentration of solid B
Bi = Biot number for external mass transfer, k_gR/D_e
D_e = effective diffusivity of gas in the pellet
J = dimensionless flux of A into the pellet
k_o = rate constant for the reaction mol/m^3/s
k_g = gas film mass transfer coefficient
r = dimensionless radial position in the pellet
R = radius of the pellet
R_A = rate of reaction, mol/s
t = time elapsed since start of reaction
x = conversion of the solid
ϕ_o = Thiele modulus of the reaction
θ = dimensionless time
λ_1 = dimensionless position of the start of the ash layer measured from the center (also the position of the end of reaction zone)
λ_2 = dimensionless position of the start of the reaction zone
ν = stoichiometric coefficient of B in the reaction

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