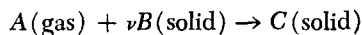


Diffusion-Controlled Rate Mechanisms in Gas-Solid Reaction Systems

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In a recent communication by Ross [*AIChE J.*, **15**, 136 (1969)], analytical solutions relating the gas concentration in a spherical solid with time were obtained for the case where the overall reaction rate equals the diffusion rate and the case where the intrinsic diffusion and reaction rates both influence the overall rate. The reaction considered was



For the case when the intrinsic diffusion in the solid is controlling the overall rate, the analytical solution obtained by Ross for a spherical particle was deduced from that for a semi-infinite solid that had been reported by Lacey, et al. [*Ind. Eng. Chem. Fundamentals*, **4**, 275 (1965)] as well as by Wen [*Ind. Eng. Chem.*, **60**, No. 9, 34 (1968)]. The purpose of the present paper is to point out the incorrectness of the solution for a spherical particle obtained by Ross as shown by his equation (9).

When the diffusion in solid is controlling the rate, the concentration of A in a spherical solid, using the notations of Ross, may be expressed as

$$\frac{\partial C_A}{\partial t} = D \left(\frac{\partial^2 C_A}{\partial r^2} + \frac{2}{r} \frac{\partial C_A}{\partial r} \right) \quad (1)$$

with boundary conditions

$$C_A(R, t) = C_{A0} \quad (2)$$

$$C_A(r', t) = 0 \quad (3)$$

$$-D \frac{\partial C_A}{\partial r} \bigg|_{r=r'} = \frac{C_{B0}}{\nu} \frac{dr'}{dt} \quad (4)$$

Equations (1), (2), and (3) can be changed into the forms

$$\frac{\partial u}{\partial t} = D \frac{\partial^2 u}{\partial \rho^2} \quad (5)$$

$$u(0, t) = C_{A0}R \quad (6)$$

$$u(\rho', t) = 0 \quad (7)$$

by the change of variables $u = C_A r$, $\rho = R - r$, and $\rho' = R - r'$. The identity of the forms of Equations (5) to (7) to those of the corresponding equations for a semi-infinite solid (with $C_{A0}R$, u , ρ and ρ' replaced, respectively, by C_{A0} , C_A , x and x') prompted Ross to suggest the moving boundary coordinate in a sphere as

$$R - r' = \sqrt{4\alpha t} \quad (8)$$

and hence the solution of Equation (1) or Equation (5) as

$$\frac{r}{R} \cdot \frac{C_A}{C_{A0}} = 1 - \frac{\operatorname{erf} \frac{R-r}{\sqrt{4Dt}}}{\operatorname{erf} \frac{R-r'}{\sqrt{4Dt}}} = 1 - \frac{\operatorname{erf} \frac{R-r}{\sqrt{4Dt}}}{\operatorname{erf} \sqrt{\frac{\alpha}{D}}} \quad (9)$$

where the constant α was stated to have the same form of relation as for the case of the semi-infinite solid. That is

$$\frac{\nu C_{A0}}{C_{B0}} \cdot \sqrt{\frac{D}{\pi\alpha}} = e^{\alpha/D} \operatorname{erf} \sqrt{\frac{\alpha}{D}} \quad (10)$$

Equation (9) is equation (9) of Ross, and Equation (10) is his equation (5) which misses a coefficient ν by misprint.

Now, if the same change of variables as made for Equations (1) to (3) is applied to Equation (4), the result is

$$\frac{-D}{r'} \frac{\partial u}{\partial \rho} \bigg|_{\rho=\rho'} = \frac{C_{B0}}{\nu} \frac{d\rho'}{dt} \quad (11)$$

The continuity requirement for a semi-infinite solid, corresponding to Equation (11), is given by equation (4) of Ross as

$$-D \frac{\partial C_A}{\partial x} \bigg|_{x=x'} = \frac{C_{B0}}{\nu} \frac{dx'}{dt} \quad (12)$$

Obviously, Equations (11) and (12) are not of identical form because the former contains r' . Therefore, the deduced solution Equation (9) cannot satisfy Equation (4) or Equation (11).

More specifically, the differentiation of Equation (9) with respect to r yields

$$\frac{\partial C_A}{\partial r} \bigg|_{r=r'} = \frac{C_{A0}R}{r' \sqrt{\pi Dt} e^{\alpha/D} \operatorname{erf} \sqrt{\frac{\alpha}{D}}} \quad (13)$$

Substituting Equation (13) into Equation (4) and integrating with the initial condition, $t = 0$, $r' = R$, gives

$$\frac{\nu C_{A0}}{C_{B0}} \cdot \sqrt{\frac{D}{\pi\alpha}} = \left(\frac{R+r'}{2R} \right) e^{\alpha/D} \operatorname{erf} \sqrt{\frac{\alpha}{D}} \quad (14)$$

Since Equation (14) contains the time-dependent variable r' , α is clearly not a constant. Thus, a characteristic equation for α similar to Equation (10) cannot be obtained.

It can be concluded that Equation (9) is not the solution of Equations (1) to (4). Although it can be shown that Equation (9) does actually satisfy Equations (1) to (3) when α is taken to be a constant, a characteristic equation for α does not exist such that Equation (4) is satisfied as well.

A Dynamical Analysis of Microbial Growth

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Monod (1), Kjeldgaard (2), Pirt (3), and many other workers have studied the growth of microbial cells primarily from the biochemical viewpoint. Recently, Tsuchiya, et al. (4), Fredrickson, et al. (5), and Ramkrishna, et al. (6) attempted dynamical analyses of microbial cell growth from the chemical engineering standpoint; they introduced

the concepts of chemical stoichiometry, mass balance, and cell age into the microbial growth reactions.

A probabilistic approach to the microbial growth by taking the individual cell age into account seems promising. However, an overall analysis of cell growth in a population by using the following two differential equations