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

$$A(\text{gas}) + \nu B(\text{solid}) \rightarrow C(\text{solid})$$

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

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

with boundary conditions

$$C_A(R, t) = C_{Ao} \tag{2}$$

$$C_A(r', t) = 0 \tag{3}$$

$$-D\left.\frac{\partial C_A}{\partial r}\right|_{r=r'} = \frac{C_{Bo}}{\nu}\frac{dr'}{dt} \tag{4}$$

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

$$\frac{\partial u}{\partial t} = D\frac{\partial^2 u}{\partial \rho^2} \tag{5}$$

$$u(0, t) = C_{Ao}R \tag{6}$$

$$u(\rho', t) = 0 \tag{7}$$

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 $C_{Ao}R$, u, ρ and ρ' replaced, respectively, by C_{Ao}, C_A, x and x') prompted Ross to suggest the moving boundary coordinate in a sphere as

$$R - r' = \sqrt{4\alpha t} \tag{8}$$

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

$$\frac{r}{R}\cdot\frac{C_A}{C_{Ao}} = 1 - \frac{\operatorname{erf}\dfrac{R-r}{\sqrt{4Dt}}}{\operatorname{erf}\dfrac{R-r'}{\sqrt{4Dt}}} = 1 - \frac{\operatorname{erf}\dfrac{R-r}{\sqrt{4Dt}}}{\operatorname{erf}\sqrt{\dfrac{\alpha}{D}}} \tag{9}$$

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

$$\frac{\nu C_{Ao}}{C_{Bo}}\cdot\sqrt{\frac{D}{\pi\alpha}} = e^{\alpha/D}\operatorname{erf}\sqrt{\frac{\alpha}{D}} \tag{10}$$

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

$$\frac{-D}{r'}\left.\frac{\partial u}{\partial \rho}\right|_{\rho=\rho'} = \frac{C_{Bo}}{\nu}\frac{d\rho'}{dt} \tag{11}$$

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

$$-D\left.\frac{\partial C_A}{\partial x}\right|_{x=x'} = \frac{C_{Bo}}{\nu}\frac{dx'}{dt} \tag{12}$$

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

$$\left.\frac{\partial C_A}{\partial r}\right|_{r=r'} = \frac{C_{Ao}R}{r'\sqrt{\pi D t}\, e^{\alpha/D}\operatorname{erf}\sqrt{\dfrac{\alpha}{D}}} \tag{13}$$

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

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

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 still deems worthy of note. Growth of micro-organisms (bacteria here in this instance) is a basis to appreciate various biochemical processes of interest.

The first equation which defines the specific growth rate μ_x of micro-organisms presents, as an approximation, a linear relation between μ_x and cellular content N_R of RNA (Ribonucleic acid).

$$\mu_x \equiv (1/X)(dX/dt) = k_2'(N_R - N_{RO}) \qquad (1)$$

The linear relationship between μ_x and N_R is justified approximately with a nitrogen-fixing bacterium as shown in Figure 1. Experimental procedures for measuring the values of μ_x and N_R in this example (*7*) are not described here for convenience.

Equation (1) has also been supported by Kjeldgaard, et al. (*2*), and others (*8* to *11*) by using various species of bacteria other than the specific one as illustrated in the figure.

In fact, a linearization of Equation (1) seems plausible, because the value of N_R ranges nearly from 5 or 6 to less than 15 or 16% in almost all the micro-organisms cultivated under different conditions. [If the value of N_R is independent of time, the growth in question is called *logarithmic,* whereas the lag of the growth suggests that N_R is a function of time (*12*).]

A mass balance of a substrate consumed, $-\Delta S$, in a culture medium is given by:

$$-\Delta S = (-\Delta S)_G + (-\Delta S)_M \qquad (2)$$

or

$$-dS/dt = (-dS/dt)_G + (-dS/dt)_M \qquad (3)$$

Perhaps one can choose any substrate for the above-mentioned mass balance, for example, carbonaceous, nitrogenous, inorganic substances, and so on in a medium. However, carbonaceous materials such as glucose, glycerol, and so forth are often adopted for ease of chemical and physiological analyses.

Yield factors $Y_{x/s}$, and Y_G are defined below to derive the second equation used in this article.

$$Y_{x/s} \equiv \Delta X/-\Delta S = \mu_x X/(-dS/dt) \qquad (4)$$

$$Y_G \equiv \Delta X/(-\Delta S)_G = \mu_x X/(-dS/dt)_G \qquad (5)$$

In addition, the last term $(-dS/dt)_M$ is assumed as follows:

$$(-dS/dt)_M = m\,X \qquad (6)$$

Substituting Equations (4), (5), and (6) into Equation (3), and rearranging

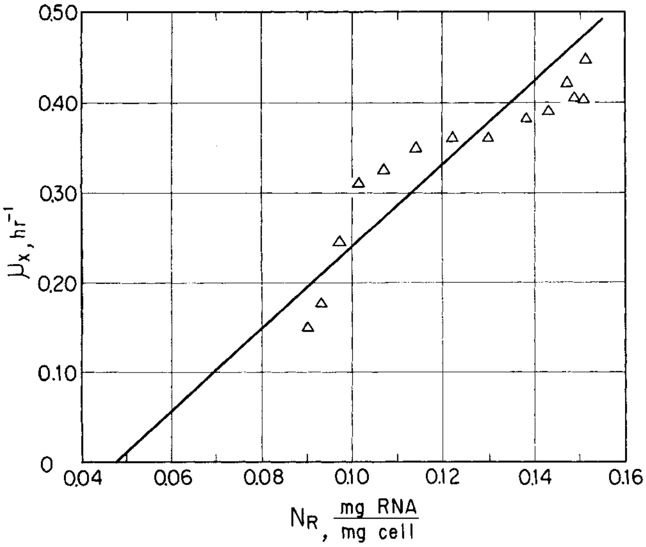

Fig. 1. μ_x vs. N_R (Azotobacter vinelandii) (*7*).

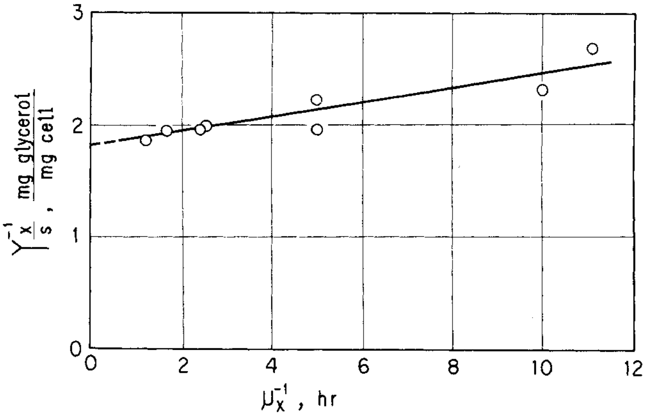

Fig. 2. $Y_{x/s}^{-1}$ vs. μ_x^{-1} (Aerobacter aerogenes; glycerol limiting) (*10*).

$$1/Y_{x/s} = 1/Y_G + m/\mu_x \qquad (7)$$

From Equations (7), (4), and (1)

$$\nu_x \equiv (1/X)(-dS/dt) = m - (k_2'N_{RO}/Y_G) + (k_2'/Y_G)\,N_R = k_3 + k_4N_R \qquad (8)$$

Equations (7) and (8) are equivalent, if Equation (1) is acceptable. Equation (7) or (8) is supported by a number of investigators (*7, 11, 13* to *15*); values of Y_G and m are dependent on the species and culture conditions of micro-organisms in respective cases. An example which justifies Equation (7) by experimentation is shown in Figure 2. [A concept of limiting substrate is applied usually in these experiments. The concentration of limiting substrate in a medium is controlled such that its increase or decrease accelerates or deteriorates appreciably the microbial growth rate; for this specific purpose, a continuous and steady state cultivation in single vessels (chemostat) is recommended.]

From Equations (1) and (8)

$$dX/dt = k_2'(N_R - N_{RO})X \qquad (1a)$$

$$-dS/dt = (k_3 + k_4N_R)X \qquad (8a)$$

In view of the experimental data (not shown here) (*7*) on a sigmoid change of N_R with time, the following equation was assumed.

$$dN_R/dt = k_1(N_R - N_{Ri} + \gamma)(N_{Rm} - N_R)$$

The unsteady state regarding N_R was concerned with the transfer from a continuous run to a batch by suspending the fresh feed and by adding delta-by-delta the substrate S into the reactor vessel to release a limited situation of the substrate.

Now, the rates of change in cell concentration X and substrate concentration S in this specific unsteady state could be represented fairly well by solving simultaneously the above-mentioned equation on N_R and Equations (8*a*) and (1*a*). In fact, values of the coefficients k_1, k_2', k_3 and k_4 could be determined with an analog computer (*7*).

Multiplying Equations (1*a*) and (8*a*) by k_3 and $k_2'N_{RO}$, respectively, and adding these equations to eliminate $N_{RO}X$ from Equation (1*a*)

$$k_3(dX/dt) - k_2'N_{RO}(dS/dt) = k_2'(k_3 + k_4N_{RO})N_RX = k_2'(k_3 + k_4N_{RO})C_R \qquad (9)$$

Differentiating both sides of Equation (8*a*) with time

$$-d^2S/dt^2 = k_3(dX/dt) + k_4(dC_R/dt) \qquad (10)$$

From Equations (9) and (10)

$$-d^2S/dt^2 - k_2'N_{RO}(dS/dt)$$

$$= k_2'(k_3 + k_4N_{RO})C_R + k_4(dC_R/dt) \qquad (11)$$

Transforming both sides of Equation (11) with the Laplace method to introduce a transfer function $G_1(p)$ defined here as the ratio of $C_R(p)$ to $-S(p)$ where p is Laplacean

$$G_1(p) \equiv \frac{C_R(p)}{-S(p)} = \frac{p^2 + k_2'N_{RO}p}{k_4p + k_2'(k_3 + k_4N_{RO})}$$

$$= \frac{1}{k_4}p - \frac{k_2'k_3}{k_4^2} + \frac{\dfrac{k^2{}_2'k_3(k_3 + k_4N_{RO})}{k_4^3}}{p + \dfrac{k_2'(k_3 + k_4N_{RO})}{k_4}}$$

$$= \frac{k_2'k_3}{k_4^2}\,\frac{k_4}{k_2'k_3}p - \frac{k_2'k_3}{k_4^2} + \frac{k_2'k_3}{k_4^2}\,\frac{\dfrac{k_2'(k_3 + k_4N_{RO})}{k_4}}{p + \dfrac{k_2'(k_3 + k_4N_{RO})}{k_4}}$$

$$= K\left(-1 + T_Dp + \frac{1}{T_Ip + 1}\right) \qquad (12)$$

Initial values of $(-dS/dt)_{t=0^+}$, $-S(t=0^+)$, and $C_R(t=0^+)$ are assumed zero; similar assumptions are made later on for $G_2(p)$ and $G_3(p)$.

Introducing another transfer function $G_2(p)$ by transforming both sides of Equation (1*a*) with the Laplace method

$$G_2(p) \equiv \frac{X(p)}{C_R(p)} = \frac{k_2'}{p + k_2'N_{RO}} = \frac{K'}{Tp + 1} \qquad (13)$$

It can be verified easily that

$$G_1(p) \cdot G_2(p) = G_3(p) \left[\equiv \frac{X(p)}{-S(p)}\right]$$

if N_R is eliminated from Equations (1*a*) and (8*a*) to derive the transfer function $G_3(p)$ accordingly.

A block diagram of the microbial growth is illustrated in Figure 3 referring to Equations (12) and (13). It is clear that a feedback involved in the synthesis of RNA starting from the substrate consumption can be either positive or negative depending on the value of T_I; naturally, the negative sign described in this context in Figure 3 assumes that the value of T_I is positive.

It is seen from Figure 3 that the first step in the microbial growth to increase the ribonucleic acid concentration C_R is represented by a PID (proportional, integral, and differential) mechanism; integral and differential mechanisms suggest, in another term, that the synthesis of C_R is controlled both by the substrate consumed up to a particular time, and by the substrate consumption rate at that time.

On the other hand, the synthesis of cell material X (protein principally) from C_R is clearly governed as shown in Figure 3 by the first-order reaction, the time constant of which is designated to T in Equation (13).

A dynamical analysis of microbial growth (bacterial growth here) which is newly attempted by introducing relevant transfer functions seems significant in the sense that the overall pattern can be envisaged from a simple diagram as shown in Figure 3, though a complete understanding of the intricate control-mechanisms inherent in this sequence of the enzymatic reactions *in vivo* is prohibitive.

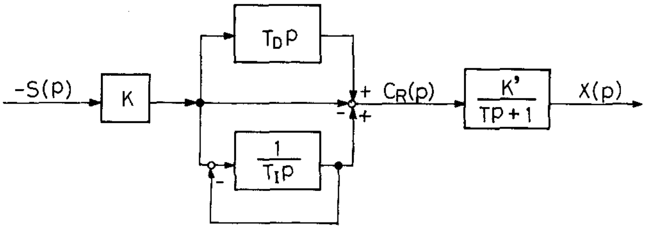

Fig. 3. Block diagram for microbial growth.

NOTATION

C_R = N_RX = concentration of RNA, mg. RNA/ml.
$G_1(p), G_2(p), G_3(p)$ = transfer functions
k_1 = empirical coefficient, hr.$^{-1}$
k_2' = empirical coefficient, hr.$^{-1}$
k_3 = $m - k_2'N_{RO}/Y_G$
k_4 = k_2'/Y_G
K = $k_2'k_3/k_4^2$
K' = $1/N_{RO}$
m = proportionality constant, hr.$^{-1}$
N_R = fraction of RNA in cells, mg. RNA/mg. cell
N_{Ri} = fraction of RNA in cells at $t = 0$, mg. RNA/mg. cell
N_{RO} = fraction of RNA in cells when $\mu_x = 0$
N_{Rm} = maximum value of N_R
p = Laplacean
S = substrate concentration, mg./ml.
t = time, hr.
T = $1/k_2'N_{RO}$
T_D = $k_4/k_2'k_3$
T_I = $k_4/k_2'(k_3 + k_4N_{RO})$
X = cell mass concentration, mg./ml.
Y_G = yield factor for growth $[\equiv \Delta X/(-\Delta S)_G]$
$Y_{x/s}$ = yield factor $(\equiv \Delta X/-\Delta S)$

Greek Letters

Δ = difference
γ = empirical constant
μ_x = specific growth rate, hr.$^{-1}$
ν_x = specific rate of substrate consumption, hr.$^{-1}$

Subscripts

G = growth
M = maintenance
x = cell mass
x/s = cell mass increased due to substrate consumed

LITERATURE CITED

1. Monod, J., *Ann. Inst. Pasteur*, **79**, 390 (1950).
2. Kjeldgaard, N. O., and C. G. Kurland, *J. Mol. Biol.*, **6**, 341 (1963).
3. Pirt, S. J., *Proc. Roy. Soc.*, **B163**, 224 (1965).
4. Tsuchiya, H. M., A. G. Fredrickson, and R. Aris, *Adv. Chem. Eng.*, **6**, 175 (1966).
5. Fredrickson, A. G., and H. M. Tsuchiya, *AIChE J.*, **9**, 459 (1963).
6. Ramkrishna, D., A. G. Fredrickson, and H. M. Tsuchiya, *J. Ferm. Technol. (Japan)*, **44**, 203, 210 (1966).
7. Nagai, S., Y. Nishizawa, I. Endo, and S. Aiba, *J Gen. Appl. Microbiol. (Tokyo)*, **14**, 121 (1968).
8. Neidhardt, F. C., and B. Magasanik, *Biochim. Biophys. Acta*, **42**, 99 (1960).
9. Rosset, R., R. Monier, and J. Julien, *Biochim. Biophys. Res. Commun.*, **15**, 329 (1964).
10. Tempest, D. W., J. R. Hunter, and J. Sykes, *J. Gen. Microbiol.*, **39**, 355 (1965).
11. ———, J. W. Dicks, and J. R. Hunter, *ibid.*, **45**, 135 (1966).
12. Aiba, S., M. Nagatani, and H. Furuse, *J. Ferm. Technol. (Japan)*, **45**, 475 (1967).
13. Schulze, K. L., and R. S. Lipe, *Archiv. fuer Mikrobiol.*, **48**, 1 (1964).
14. Harte, M. J., and F. C. Webb, *Biotech. Bioeng.*, **9**, 205 (1967).
15. Herbert, D., R. Elsworth, and R. C. Telling, *J. Gen. Microbiol.*, **14**, 601 (1956).