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Analytical Solution for a First-Order Reaction in a Packed Bed with Diffusion

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An analytical solution for a packed bed reactor with a first-order reaction is important in reactor analysis. Transient-state solutions for a reactive adsorbate in a packed bed relate closely to the solutions for nonreactive adsorbates. Rosen (1952) derived a solution for the breakthrough curve for a nonreactive adsorbate with both interfacial and intraparticle diffusional resistances. Rasmuson and Neretnieks (1980) extended the model of Rosen to include longitudinal dispersion; however, they chose the first Bromwich path of integration for inverting the Laplace transform of a function with branch points. In this paper, we choose the second Bromwich path in order to derive the transient solution for a gas sample flowing through a packed bed where a first-order reaction takes place in the solid phase. The solution for a radioactive gas can be generalized from our solution, and the solution for a nonreactive gas is a simplification of our solution.

The differential equations, which describe the gas-phase concentration C and the solid-phase concentration q, are written as

$$\frac{\partial C}{\partial t} + u\frac{\partial C}{\partial z} - D_L\frac{\partial^2 C}{\partial z^2} = -\frac{1-\epsilon}{\epsilon}\frac{\partial \overset{\Delta}{q}}{\partial t} - \frac{1-\epsilon}{\epsilon}\lambda\overset{\Delta}{q} \qquad (1)$$

and

$$\frac{\partial q}{\partial t} = D_s\left(\frac{\partial^2 q}{\partial r^2} + \frac{2}{r}\frac{\partial q}{\partial r}\right) - \lambda q \qquad (2)$$

Here we assumed that the gas-phase concentration does not change significantly over a distance equal to a diameter of the catalyst pellets. This assumption was discussed by Babcock et al. (1966). The average solid-phase concentration $\overset{\Delta}{q}$ for spherical pellets is given by

$$\overset{\Delta}{q} = \frac{3}{R^3}\int_0^R q(r,z,t)r^2dr \qquad (3)$$

The introduction of an average concentration eliminates the radial dependence of the solid-phase concentration from Eq. 1.

The initial and boundary conditions are written as

$$C(0,t) = C_0 \qquad (4)$$

$$C(\infty,t) = 0 \qquad (5)$$

$$C(z,0) = 0 \qquad (6)$$

$$q_i(0,z,t) \neq \infty \qquad (7)$$

$$q_i(R,z,t) = q_s(z,t) \text{ given by } \frac{\partial \overset{\Delta}{q}}{\partial t} = \frac{3k_f}{R}\left(C - \frac{q_s}{K}\right) - \lambda\overset{\Delta}{q} \qquad (8)$$

$$q_i(r,z,0) = 0 \qquad (9)$$

Equations 2 through 9 can be solved formally using Duhamel's theorem for arbitrary concentrations $q_s(z,t)$ on the surface of the pellets:

$$q(r,z,t) = \int_0^t q_s(z,\tau)\frac{\partial}{\partial t}F(r,t-\tau)d\tau \qquad (10)$$

where $F(r,t)$ is the solution of Eq. 2 for a step increase of the concentration at the surface of the pellets (i.e., $r = R$). Then substituting Eq. 10 into Eq. 3 and performing the integration over r, we obtain

$$\overset{\Delta}{q} = \frac{3}{R^3}\int_0^R\int_0^t q_s(z,\tau)\frac{\partial}{\partial t}F(r,t-\tau)r^2d\tau dr \qquad (11)$$

Taking the Laplace transform of Eqs. 8 and 11, we have

$$s\tilde{\overset{\Delta}{q}} = \frac{3k_f}{R}\left(\tilde{C} - \frac{\tilde{q}_s}{K}\right) - \lambda\tilde{\overset{\Delta}{q}} \qquad (12)$$

and

$$\tilde{\overset{\Delta}{q}} = \frac{3}{R^3}\int_0^R q_s(z,\tau)\frac{R}{r}\frac{\sinh r\sqrt{\dfrac{\lambda+s}{D_s}}}{\sinh R\sqrt{\dfrac{\lambda+s}{D_s}}}r^2dr \qquad (13)$$

$$= \frac{3D_s\tilde{q}_s(z,\tau)}{R^2(\lambda+s)}\left(R\sqrt{\frac{\lambda+s}{D_s}}\coth R\sqrt{\frac{\lambda+s}{D_s}} - 1\right) \qquad (14)$$

Again, taking the Laplace transform of Eq. 1 and using Eqs. 13 and 14 to eliminate $\tilde{q}_s$ and $\tilde{\overset{\Delta}{q}}$, we have

$$\frac{\partial^2\tilde{C}}{\partial z^2} - \frac{u}{D_L}\frac{\partial\tilde{C}}{\partial z} - \left(\frac{s}{D_L} + \frac{Y_T(s)}{mD_L}\right)\tilde{C} = 0 \qquad (15)$$

where

$$Y_T(s) = \frac{Y_D(s)}{1 + R_FY_D(s)} \qquad (16)$$

$$Y_D(s) = \frac{3K(s+\lambda)}{\sigma^2}(\sigma\coth\sigma - 1) \qquad (17)$$

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$$\sigma = R\sqrt{\frac{s+\lambda}{D_s}} \tag{18}$$

$$R_F = \frac{R}{3k_f} \tag{19}$$

$$m = \frac{\epsilon}{1-\epsilon} \tag{20}$$

Equation 15 is a homogeneous second-order linear differential equation. The solution is

$$\frac{\tilde{C}(z,s)}{C_0} = \frac{1}{s}\exp\left(\frac{uz}{2D_L} - z\sqrt{Y_A(s)}\right) \tag{21}$$

where

$$Y_A(s) = \frac{u^2}{4D_L^2} + \frac{s}{D_L} + \frac{Y_T(s)}{mD_L} \tag{22}$$

The properties of the functions $Y_T(s)$ and $Y_A(s)$ were discussed by Rosen (1952) and by Rasmuson and Neretnieks (1980). The function $Y_T(s)$ has an infinite number of singularities on the negative real axis. These singularities are defined by the following relation

$$R_F Y_D(-\xi_n) + 1 = 0 \tag{23}$$

Note that $Y_A(s)$ changes sign in the neighborhood of each $-\xi_n$; therefore, the ξ_n's are branch points. Another set of branch points are the roots $-\eta_n$ of $Y_A(s)$:

$$Y_A(-\eta) = 0 \tag{24}$$

Between two successive singularities $-\xi_{n-1}$ and $-\xi_n$, the value of $Y_A(s)$ ranges from $+\infty$ to $-\infty$; therefore, from Eq. 22, there is a root of $-\eta_n$ between two successive singularities.

The properties of $\tilde{C}(z,s)$ can be discussed as follows: For $s > 0$, $\tilde{C}$ is analytic. At $s = 0$, $\tilde{C}$ is a simple pole. When $s < 0$, $\tilde{C}$ is analytic on the real axis until the first root $-\eta_1$ of $Y_A(s)$, where $Y_A(s)$ becomes negative. Because the square-root sign in Eq. 21 causes $\tilde{C}$ to be a multi-valued function, the negative real axis to the left of $-\eta_1$ becomes a branch cut. The branch cut has finite length because it terminates at the first singularity $-\xi_1$ where $Y_A(s)$ turns positive again. The function $\tilde{C}$ becomes analytic again until the argument s reaches the second root of $Y_A(s)$. This process repeats throughout the negative real axis to $-\infty$ resulting in an infinite number of piecewise cuts.

In order to invert the Laplace transform $\tilde{C}$, we choose a second Bromwich path of integration. Following McLachlan (1963), we choose integration paths which exclude all finite cuts. One such path surrounds the cut between $-\eta_1$ and $-\xi_1$; for this case, the integration path first makes a small circle around $-\eta_1$, then moves below real axis from $-\eta_1$ to $-\xi_1$, then makes a small circle around $-\xi_1$, and finally moves above the real axis back to $-\eta_1$ to form a closed loop. Each one of these integration paths contributes to the inverse Laplace transform of Eq. 21:

$$\frac{1}{2\pi i}\left[\int_{\eta_n} + \int_{-\eta_n}^{-\xi_n} + \int_{-\xi_n} + \int_{-\xi_n}^{-\eta_n}\right]\frac{1}{s}e^{st - z\sqrt{Y_A(s)}}\,ds \tag{25}$$

By letting $s = -\eta_n + \epsilon e^{i\theta}$ and noting that $Y_A(-\eta_n) = 0$, we have

$$\frac{1}{2\pi i}\int_{-\eta_n} = \lim_{\epsilon\to 0}\int_{-\pi}^{-\pi}\frac{\epsilon}{2\pi\eta_n}e^{-\eta_n t}e^{i\theta}d\theta = 0 \tag{26}$$

The third integral of Eq. 25 also vanishes because $\tilde{C} = 0$ at $s = -\xi_n$. The second and the fourth integrals in Eq. 25 can be combined by letting $s = xe^{i\pi}$ in the second integral and $s = xe^{-i\pi}$ in the fourth integral. Then, the integration becomes

$$\int_{\eta_n}^{\xi_n}\frac{e^{-xt - zi\sqrt{|Y_A(-x)|}}}{2\pi ix}dx + \int_{\xi_n}^{\eta_n}\frac{e^{-xt + zi\sqrt{|Y_A(-x)|}}}{2\pi ix}dx$$
$$= \frac{-1}{\pi}\int_{\eta_n}^{\pi_n}\frac{e^{-xt}}{x}\sin\left(z\sqrt{\frac{x}{D_L} - \frac{Y_T(-x)}{mD_L} - \frac{u^2}{4D_L^2}}\right)dx \tag{27}$$

Here the absolute value of Y_A is taken because Y_A is negative between the two limits. By summing the results of integration around each cut, and also by taking the residue at $s = 0$, we obtain

$$T \equiv \frac{C(z,t)}{C_0} = \exp\left(\frac{uz}{2D_L} - z\sqrt{Y_A(0)}\right) - \sum_{n=1}^{\infty}\frac{1}{\pi}\int_{\eta_n}^{\xi_n}\frac{e^{uz/2D_L - xt}}{x}$$
$$\times \sin\left(z\sqrt{\frac{x}{D_L} - \frac{Y_T(-x)}{mD_L} - \frac{u^2}{4D_L}}\right)dx \tag{28}$$

$$= \exp\left(\frac{uz}{2D_L} - z\sqrt{Y_A\ (0)}\right) - \frac{1}{\pi}\int_0^{\infty}\frac{e^{uz/2D_L - xt}}{x}$$
$$\times \sin\left(z\sqrt{|Y_A|}\right)\left(\frac{1 - sgn(Y_A)}{2}\right)dx \tag{29}$$

where $sgn(Y_A)$ is 1 when $Y_A \geq 0$ and is -1 when $Y_A < 0$.

Equation 28 can be generalized to the case of a decaying radioactive isotope by adding λ/D_L to the definition of $Y_A(s)$ in Eq. 22. The solution for a nonreactive adsorbate also follows from Eq. 28 by letting $\lambda = 0$ in Eq. 16 for Y_D. When $t \to \infty$, all integrations of Eq. 28 vanish leaving only the first term; in this case, the expression for the output concentration depends on the longitudinal dispersion coefficient D_L and the efficiency factor of the catalyst pellets. Underhill (1969) described this dependence for the steady-state case.

In their paper, Rasmuson and Neretnieks (1980) use the same integration path chosen by Rosen (1952) to invert the Laplace transform. The path they use is the first Bromwich contour. Rasmuson and Neretnieks (1980) use de Moivre's theorem to evaluate a square root of an expression similar to that in Eq. 21; however, they include only the principal root. Since their procedure treats the whole complex plane as analytical, it invalidates the use of the first Bromwich path because of the existence of branch points; otherwise, as discussed, for example, by McLachlan (1963), the first and second Bromwich paths would give the same result since the value of the integral vanishes over the contour at infinity. Rasmuson and Neretnieks (1980) show also that their solution reduces to that of Rosen (1952) when $D_L \to 0$. This agreement is not a test of their method because the square-root term becomes algebraic when $D_L \to 0$ and the first Bromwich path is valid. For the case of finite D_L and infinite D_s and k_f, the solution using the second Bromwich path can be simplified to the solution of Lapidus and Amundson (1952). With an assumption of a nonreactive adsorbate ($\lambda = 0$), we have

$$Y_A(-x) = -\left(\frac{K}{m} + 1\right)\frac{x}{D_L} + \frac{u^2}{4D_L^2} \tag{30}$$

From this expression for Y_A, there is only one root η:

$$\eta = \frac{u^2}{4D_L\left(\frac{K}{m} + 1\right)} \tag{31}$$

The integration in Eq. 28 extends from this root to infinity. Thus, Eq. 28 becomes

$$T = 1 - \frac{1}{\pi}\int_{\eta}^{\infty}\frac{e^{1/2\Delta - xt}}{x}\sin\left[(2\Delta)^{-1}\sqrt{(x/\eta) - 1}\right]dx \tag{32}$$

where we define

$$\Delta \equiv \frac{D_L}{uz} \tag{33}$$

Introducing the variable θ

$$\theta = (2\Delta)^{-1}\sqrt{(x/\eta) - 1} \tag{34}$$

Equation 32 becomes

$$T = 1 - \frac{2}{\pi}\exp\left(\frac{1}{2\Delta} - \eta t\right)$$
$$\times \int_0^{\infty}\frac{\theta\exp(-4\eta t\Delta^2\theta^2)\sin\theta d\theta}{\theta^2 + \frac{1}{4\Delta^2}} \tag{35}$$

This equation can be further simplified to

$$T = \frac{1}{2} \exp\left(\frac{1}{\Delta}\right) \operatorname{erfc}\left(\frac{1}{2\Delta}\sqrt{\frac{1}{\eta t}} + \sqrt{\eta t}\right) + \frac{1}{2} \operatorname{erfc}\left(\frac{1}{2\Delta}\sqrt{\frac{1}{\eta t}} - \sqrt{\eta t}\right) \quad (36)$$

This is the solution of Lapidus and Amundson (1952).

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NOTATION

C = concentration in fluid, mol/m^3
C_o = inlet concentration in fluid, mol/m^3
D_L = longitudinal dispersion coefficient, m^2/s
D_S = diffusivity in solid phase, m^2/s
K = volume equilibrium constant, m^3/m^3
k_f = mass transfer coefficient, m/s
m = $\epsilon/(1-\epsilon)$
$\overset{\Delta}{q}$ = volume averaged concentration in particles, mol/m^3
q = internal concentration in particles, mol/m^3
q_s = $q_i(R,z,t)$, mol/m^3
R = particle diameter, m
R_F = $R/3k_f$, film resistance, s
r = radial distance from center of spherical particle, m
s = Laplace transform variable
t = time, s
T = C/C_o, dimensionless concentration in fluid
u = average linear flow velocity, m/s
x = variable of integration
z = distance in flow direction, m

Greek Letters

α_n = $n\pi/R$, s^{-1}
σ = $R\sqrt{\frac{s+\lambda}{D_s}}$
ϵ = porosity, m^3/m^3
λ = reaction rate constant, s^{-1}

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A Group Contribution Molecular Model of Liquids and Solutions

Part III: Groups and Interactions in Aromatics, Cycloparaffins, Ethers Amines, and Their Solutions

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Group contribution models permit predictions for a large number of molecular systems, provided that the properties of a small number of groups are known. According to the molecular model of group contributions developed by Nitta et al. (1977), properties of pure liquid paraffins, alcohols, ketones, and their solutions, including activity coefficients and heats of mixing, can be efficiently predicted based on four groups (Ch$_3$, CH$_2$, CO, OH) and their interactions. Chien et al. (1981) have recently shown that this model successfully describes water and aqueous solutions of nonelectrolytes. In this communication we report extension of the model by Nitta et al. (1977) to aromatics, cycloalkanes, di-alkylethers, primary amines, and their solutions. Parameter values are presented for five additional groups.

CORRECTION FOR ENTROPY EFFECT OF RING ELEMENTS

In applying the Nitta model to ring-containing molecules such as the aromatic and cycloalkane hydrocarbons, we have found it necessary to introduce a correction to their core volumes for use in the Flory-Huggins entropy formula