Adsorption Rate Studies—Interaction of Diffusion and Surface Processes

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The adsorption of a component of a gas mixture on a solid particle can be described by a three-step mechanism: diffusion from the main body of the gas phase to the external surface of the particle, diffusion into the particle (for example through the pore volume, or by migration along the solid surface of the pore in a porous particle, and by a solid diffusion mechanism in an impermeable particle), and adsorption on the pore surface. In the general case all three steps can contribute to the overall rate measured in terms of concentrations in the bulk gas stream.

The application of adsorption rates generally involves an assembly of solid particles such as a fixed bed through which the gas flows. The desired result is usually the concentration of the adsorbate in the gas leaving the bed as a function of time. Based upon reasonable assumptions, analytical solutions have been obtained when the overall rate is determined by but one of the three steps. For example for surface adsorption or external diffusion controlling the rate Nusselt (*7*), Anzelius (*2*), and others (*5, 11*) have presented equivalent mathematical developments. Thomas (*12*), Rosen (*8*), and Edeskuty and Amundson (*4*) all solved the problem when only intraparticle diffusion is significant.

Previous theoretical treatment to include the resistances of two of the three steps is limited to that of Rosen (*9*) who considered the combined effects of intraparticle and external diffusion. Later in this paper solutions are reported for the additional two-resistance cases of intraparticle diffusion-surface adsorption and external diffusion-surface adsorption. A solution of the general three-resistance case in integral form has also been developed (*6*). In view of the previous papers presenting specific solutions and the new results of this work it is desirable to summarize in one place the status of the problem. Hence the initial equations, assumptions, and solutions are given in Table 1 for several variations of the problem of concentration as a function of time in the gas phase leaving a fixed bed of porous particles.

In the second paper experimental data for the adsorption of ethyl alcohol on silica gel are analyzed with the mathematical solutions to determine the significance of specific resistances.

INITIAL EQUATIONS AND ASSUMPTIONS

A gas mixture containing a single adsorbable component flows through a bed of solid particles under isothermal and isobaric conditions at a constant superficial velocity u. The particles are spherical (radius = R) and form a bed of length z_o. The concentration of adsorbate in the entering stream is $\overline{C}_o$. The major assumptions upon which the following equations are based are:

1. The adsorption is proportional to the gas-phase concentration and independent of the fraction of the surface covered with adsorbate. Thus the equilibrium relationship between adsorbed molecules and those in the gas phase is linear. This is a reasonable assumption for small concentrations.
2. Axial diffusion in the bed is negligible with respect to bulk flow.
3. Concentration gradients in the radial direction in the gas phase are negligible.

With these restrictions the concentration $\overline{C}(z, \theta)$ is determined by the following seven equations:

Mass balance in gas phase

$$u\frac{\delta \overline{C}}{\delta z} + \epsilon_B \frac{\delta \overline{C}}{\delta \theta} + \tilde{R} = 0 \tag{1}$$

Mass balance in particle

$$D_i\left(\frac{\delta^2 C}{\delta r^2} + \frac{2}{r}\,\frac{\delta C}{\delta r}\right) = \epsilon_p \frac{\delta C}{\delta \theta} + \rho_p \frac{\delta S}{\delta \theta} \tag{2}$$

Surface rate

$$\frac{\delta S}{\delta \theta} = \overset{\rightarrow}{\lambda}\, C - \overset{\leftarrow}{\mu}\, S = \overset{\rightarrow}{\lambda}\left(C - \frac{1}{\lambda_e} S\right) \tag{3}$$

External diffusion, boundary condition

$$k_f\,(\bar{C} - C) = D_i\left(\frac{\delta C}{\delta r}\right)_{r=R} \tag{4}$$

Rate of diffusion $\tilde{R}$

$$\tilde{R} = 4\,\pi\,R^2\,\bar{n}\,D_i\left(\frac{\delta C}{\delta r}\right)_{r=R} = \frac{3\rho_B}{\rho_p}\left(\frac{D_i}{R}\right)\left(\frac{\delta C}{\delta r}\right)_{r=R} \tag{5}$$

where $\bar{n}$ is the number of spherical particles per unit volume of bed, $\bar{n} = \rho_B/(4/3\,\pi\,R^3\,\rho_p)$.

Initial condition and boundary condition

$$C = \overline{C} = S = 0, \quad \text{at } \theta = 0; \quad z_o \geqq z \geqq 0 \tag{6}$$

$$\overline{C} = \overline{C}_o \ \text{ at } z = 0, \quad \theta \geqq 0 \tag{7}$$

The solution can be simplified by replacing variables z and θ by x and t in accordance with the expressions

$$x = \frac{z\epsilon_B}{u} \tag{8}$$

$$t = \theta - \frac{z\epsilon_B}{u} \tag{9}$$

When one uses Equation (5) for $\tilde{R}$, the change of variables reduces Equations (1), (2), (3), (6), and (7) to the form

$$\frac{\delta \bar{C}}{\delta x} + \frac{3\rho_B}{\epsilon_B \rho_p}\frac{D_i}{R}\left(\frac{\delta C}{\delta r}\right)_{r=R} = 0 \tag{10}$$

$$D_i\left(\frac{\delta^2 C}{\delta r^2} + \frac{2}{r}\frac{\delta C}{\delta r}\right) = \epsilon_p\left(\frac{\delta C}{\delta t}\right) + \rho_p\left(\frac{\delta S}{\delta t}\right) \tag{11}$$

$$\frac{\delta S}{\delta t} = \overset{\rightarrow}{\lambda}\, C - \overset{\leftarrow}{\mu}\, S \tag{12}$$

$$C = \bar{C} = 0,\ S = 0 \text{ at } t = \frac{z\epsilon_B}{u} \cong 0; \quad x_o \geqq x \geqq 0 \tag{13}$$

$$\bar{C} = \bar{C}_o \text{ at } x = 0 \quad t \geqq -\frac{z\epsilon_B}{u} \cong 0 \tag{14}$$

In Equations (13) and (14) the time interval $z\epsilon_B/u$ corresponds to the holdup time in the bed and is usually negligible with respect to the time required for finite adsorption.

The solution of Equations (4), (5), (10), (11), (12), (13), and (14) can be obtained in terms of dimensionless groups, the number of which depends upon the resistances included. When all three resistances are retained, four groups are involved (*6*). The numerical work in evaluating the solution over a range of the four parameters is considerable. Frequently this is not necessary because one or more of the resistances is negligible. For small particles the overall rate is often determined by intraparticle and surface reaction resistances. This case is solved in the next section. Since only three dimensionless parameters are needed, it does not require excessive calculations to evaluate numerically the solution (to obtain $\bar{C}/\bar{C}_o$ at z_o) for a range of values of the parameters. Then the mathematical solutions for the other two-resistance cases are presented. Also included are new solutions for the single-resistance problems in terms of the same parameters (but two are necessary for these cases). These results agree with the earlier solutions (*2, 5, 7, 11*) and are simpler to use.

INTRAPARTICLE DIFFUSION AND SURFACE ADSORPTION

The system for this case is described by Equations (10), (11), (12), (13), (14), (5) and the form of Equation (4) which is applicable for negligible external diffusion resistance; that is

$$C - \bar{C} = 0 \text{ at } r = R \tag{15}$$

The method of solution employed is to apply a double Laplace transform (*3*) to the variables x and t. This approach follows that used by Amundson (*1, 4*) for problems involving diffusion resistances but no surface rate resistance. The symbols used for the transformation are:

$$\mathcal{L}_x\,[C(x,t,r)] = \int_0^\infty e^{-px}\,C\,dx = f(r,p,t) = f_x \tag{16}$$

$$\mathcal{L}_t\,[C(x,t,r)] = \int_0^\infty e^{-qt}\,C\,dt = f(r,x,q) = f_t \tag{17}$$

$$\mathcal{L}_{xt}\,[C(x,t,r)] = \int_0^\infty\int_0^\infty e^{-(px+qt)}\,C\,dxdt = f(r,p,q) = f_{xt} \tag{18}$$

$$\mathcal{L}_x[S(x,t,r)] = \int_0^\infty e^{-px}\,S\,dx = g(r,p,t) = g_x \tag{19}$$

$$\mathcal{L}_t[S(x,t,r)] = \int_0^\infty e^{-qt}\,S\,dt = g(r,x,q) = g_t \tag{20}$$

$$\mathcal{L}_{xt}[S(x,t,r)] = \int_0^\infty\int_0^\infty e^{-(px+qt)}\,S\,dxdt = g(r,p,q) = g_{xt} \tag{21}$$

and for the interparticle gas concentration $\bar{C}$

$$\mathcal{L}_x\,[\bar{C}(x,t)] = \int_0^\infty e^{-px}\,\bar{C}\,dx = F(p,t) = F_x \tag{22}$$

$$\mathcal{L}_t\,[\bar{C}(x,t)] = \int_0^\infty e^{-qt}\,\bar{C}\,dt = F(x,q) = F_t \tag{23}$$

$$\mathcal{L}_{xt}\,[\bar{C}(x,t)] = \int_0^\infty\int_0^\infty e^{-(px+qt)}\,\bar{C}\,dx\,dt = F(p,q) = F_{xt} \tag{24}$$

Using the relation for the transform of the first derivative, and applying the initial condition [Equation (13)] one obtains

$$\mathcal{L}_x\left[\mathcal{L}_t\left(\frac{dC}{dt}\right)\right] = \mathcal{L}_x \quad [C\,e^{-qt}]_0^\infty + q\int_0^\infty C\,e^{-qt}\,dt \quad = \mathcal{L}_x\,\{q\,f_t\} = q\,f_{xt} \tag{25}$$

Similarly for the variables S and $\bar{C}$, when one utilizes the boundary conditions of Equation (14)

$$\mathcal{L}_x\left[\mathcal{L}_t\left(\frac{\delta S}{\delta t}\right)\right] = q\ g_{xt} \tag{26}$$

$$\mathcal{L}_t\left[\mathcal{L}_x\left(\frac{\delta \bar{C}}{\delta x}\right)\right] = \mathcal{L}_t\,[\bar{C}_o + p\,F_x] = -\frac{\bar{C}_o}{q} + p\,F_{xt} \tag{27}$$

Now application of the double transform procedure to Equations (10), (11), (12), and (15) reduces the problem to the solution of the following set of ordinary differential and algebraic equations:

$$-\frac{\bar{C}_o}{q} + p\,F_{xt} + C_1\left(\frac{df_{xt}}{dr}\right)_{r=R} = 0 \tag{28}$$

where

$$C_1 = \frac{3\rho_B}{\epsilon_B\rho_p}\left(\frac{D_i}{R}\right) \tag{29}$$

$$D_i\left(\frac{d^2 f_{xt}}{dr^2} + \frac{2}{r}\frac{df_{xt}}{dr}\right) = q\,(\epsilon_p\,f_{xt} + \rho_p\,q_{xt}) \tag{30}$$

$$q\ g_{xt} = \overset{\rightarrow}{\lambda}\ f_{xt} - \overset{\leftarrow}{\mu}\ q_{xt} \tag{31}$$

$$(F_{xt})_{r=R} = (f_{xt})_{r=R} \tag{32}$$

Combination of Equations (30) and (31) gives the following equation in f_{xt}:

$$\frac{d^2 f_{xt}}{dr^2} + \frac{2}{r}\,\frac{d f_{xt}}{dr} - \frac{q\left(\epsilon_p + \dfrac{\rho_p \overrightarrow{\lambda}}{q + \overleftarrow{\mu}}\right)}{D_i} f_{xt} = 0$$

Since ϵ_p is negligible with respect to $(\overrightarrow{\lambda}\,\rho_p)/(q + \overleftarrow{\mu})$, the equation may be written as

$$\frac{d^2 f_{xt}}{dr^2} + \frac{2}{r}\,\frac{d f_{xt}}{dr} - \frac{\rho_p \overrightarrow{\lambda}}{D_i}\,\frac{q}{q + \overleftarrow{\mu}}\, f_{xt} = 0 \qquad (33)$$

The general solution of Equation (33) is

$$f_{xt} = \frac{C_2}{r}\sin\left(r\sqrt{\frac{-\rho_p\overrightarrow{\lambda}}{D_i}\cdot\frac{q}{q + \overleftarrow{\mu}}}\right) + \frac{C_3}{r}\cdot\cos\left(r\sqrt{\frac{-\rho_p\overrightarrow{\lambda}}{D_i}\cdot\frac{q}{q + \overleftarrow{\mu}}}\right)$$

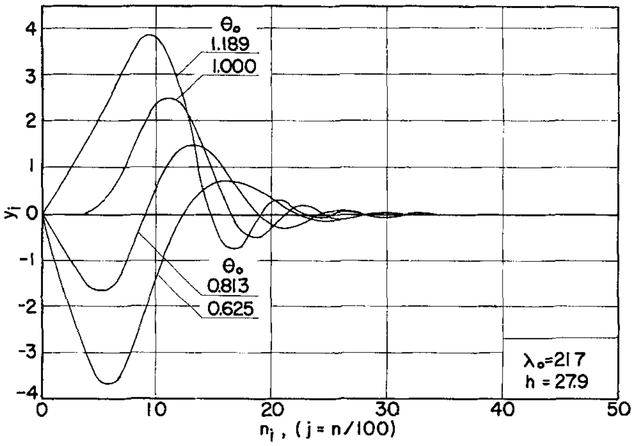

Fig. 1. Convergence of $y(\lambda)$.

However the constant C_3 must vanish since f_{xt} should be finite at $r = 0$. Hence the solution reduces to

$$f_{xt} = \frac{C_2}{r}\sin\left[\frac{r\,h\,W(q)}{R}\right] \qquad (34)$$

where $W(q)$ and h are defined by the expressions

$$W(q) = i\sqrt{\frac{q}{q + \overleftarrow{\mu}}} \qquad (35)$$

$$h = R\sqrt{\frac{\overrightarrow{\lambda}\rho_p}{D_i}} \qquad (36)$$

The constant C_2 can be evaluated from Equations (28) and (32). The result is

$$C_2 = \frac{\overline{C}_o R}{q}\,\frac{1}{\sin\left[h\,W(q)\right]}\;\frac{1}{p + \dfrac{C_1}{R}\{h\,W(q)\cot\left[h\,W(q)\right] - 1\}} \qquad (37)$$

Then the solution for f_{xt} becomes

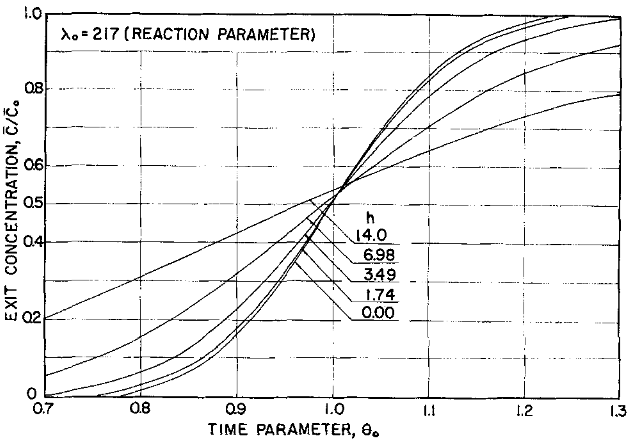

Fig. 2. Effect of diffusion group *h* on breakthrough curve.

$$f_{xt} = \frac{R\overline{C}_o}{rq}\,\frac{\sin\dfrac{r\,h\,W(q)}{R}}{\sin\left[h\,W(q)\right]}\;\frac{1}{p + \dfrac{C_1}{R}\{h\,W(q)\cot\left[h\,W(q)\right] - 1\}} \qquad (38)$$

The next step is to use the inverse transform to obtain f_t from Equation (38). Then Equation (10) is transformed with respect to t, obtaining an ordinary differential equation in dF_t/dx and involving df_t/dr. This may be solved for F_t. Then the inverse transform gives the required solution for $\overline{C}$ as a function of x and t [Equation (23)]. Carrying out these steps one can apply the inverse transform relationship

$$\mathcal{L}^{-1}\left[\frac{1}{p + a}\right] = e^{-ax} \qquad (39)$$

in Equation (38) to obtain

$$f_t = \frac{R\overline{C}_o}{q}\,\frac{\sin\dfrac{rh\,W(q)}{R}}{\sin\left[h\,W(q)\right]}\;\exp\left[-\frac{C_1}{R}x\,\{h\,W(q)\cot\left[h\,W(q)\right] - 1\}\right] \qquad (40)$$

Now transforming Equation (10) with respect to t one gets

$$\frac{dF_t}{dx} + C_1\left(\frac{df_t}{dr}\right)_{r=R} = 0 \qquad (41)$$

The term $(df_t/dr)_{r=R}$ can be evaluated from Equation (40). If this is done, and the result integrated, there is obtained

$$F_t = \frac{\overline{C}_o}{q}\exp\left[-\frac{C_1}{R}x\,\{h\,W(q)\cot\left[h\,W(q)\right] - 1\}\right] \qquad (42)$$

Now the solution may formally be written as the inverse transform of Equation (42); that is

$$\overline{C}(x, t) = \frac{1}{2\pi i}\lim_{\beta\to\infty}\left[\int_{\gamma - iB}^{\gamma + iB} e^{qt}\,F_t\,dq\right] \qquad (43)$$

The function F_t has a single pole at $q = 0$ and an infinite number of unessential singularities on the negative side of the real axis. Hence it is not practical to evaluate the integral in Equation (43) by the method of summing

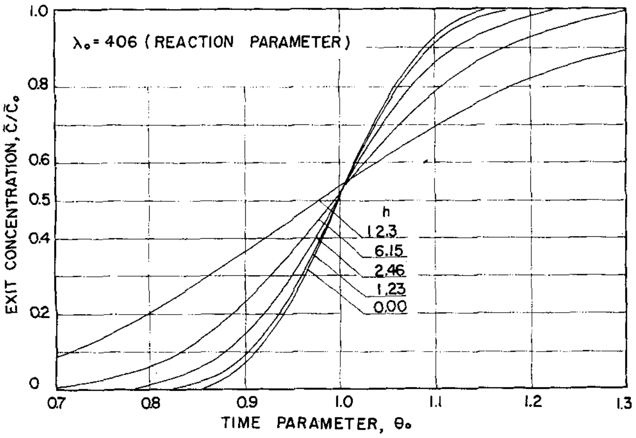

Fig. 3. Effect of diffusion group *h* on breakthrough curve for high value of reaction group λ_o.

the residues. However by substituting $\frac{q}{\overleftarrow{\mu}} = \frac{i\beta}{\overleftarrow{\mu}} = \lambda^2$, it is possible (*3, 8*) to transform the integral into a real, improper form. In this manner Equation (43) can be written in terms of the integration parameter λ as follows:

$$\frac{\overline{C}}{\overline{C}_o} = \frac{1}{2} + \frac{2}{\pi}\int_o^\infty e^{-\frac{C_1}{R} x\,\psi_1(\lambda)} \sin\left[\overleftarrow{\mu}\,t\,\lambda^2 - \frac{C_1}{R}\,x\,\psi_2(\lambda)\right]\frac{d\lambda}{\lambda} \tag{44}$$

where

$$\psi_1(\lambda) = \left[\frac{\Phi_1(\lambda)\,\sin 2\Phi_1(\lambda) + \Phi_2(\lambda)\,\sinh 2\,\Phi_2(\lambda)}{\cosh 2\,\Phi_2(\lambda) - \cos 2\,\Phi_1(x)} - 1\right] \tag{45}$$

$$\psi_2(\lambda) = \left[\frac{\Phi_2(\lambda)\sin 2\,\Phi_1(\lambda) - \Phi_1(\lambda)\,\sinh 2\,\Phi_2(\lambda)}{\cosh 2\,\Phi_2(\lambda) - \cos 2\,\Phi_1(\lambda)}\right] \tag{46}$$

and

$$\Phi_1(\lambda) = -h\,\lambda\left[\frac{1}{2(\lambda^4+1)(\sqrt{\lambda^4+1}+\lambda^2)}\right]^{1/2} \tag{47}$$

$$\Phi_2(\lambda) = h\,\lambda\left[\frac{1}{2(\lambda^4+1)(\sqrt{\lambda^4+1}-\lambda^2)}\right]^{1/2} \tag{48}$$

Equation (44) can be evaluated numerically to give curves of $\overline{C}/\overline{C}_o$ vs. x and t, or the original variables θ and z. Actually what is desired is $\overline{C}/\overline{C}_o$ at z_o or $x_o = z_o\epsilon_B/\mu$, corresponding to the exit of the bed. Before obtaining this it is advantageous to generalize Equation (44) by expressing it in terms of three dimensionless groups:

Intraparticle diffusion group

$$h = R\sqrt{\frac{\overrightarrow{\lambda}\cdot\rho_p}{D_i}} \tag{36}$$

Reaction group

$$\lambda_o = \theta_\infty\,\overleftarrow{\mu} = \frac{\theta_\infty}{\lambda_e}\overrightarrow{\lambda} \tag{49}$$

Time group

$$\theta_o = \frac{\theta}{\theta_\infty} \tag{50}$$

The quantity θ_∞ depends upon z_o. It is the time required for the concentration $\overline{C}$ at z_o to reach $\overline{C}_o$, if the overall adsorption rate were infinite. For an infinite rate the curves of $\overline{C}_{zo}$ vs. θ would be a step function, that is $\overline{C}_{zo} = 0$ from $\theta = 0$ to θ_∞ and $\overline{C}_{zo} = \overline{C}_o$ for $\theta > \theta_\infty$. Hence θ_∞ is simply related to the properties of the bed by the expression

$$\theta_\infty\,u\,\overline{C}_o = \text{max adsorbable (equilibrium with } \overline{C}_o\text{) in the bed}$$

$$= \rho_B\,z_o\,(\lambda_e\overline{C}_o)$$

or

$$\theta_\infty = \frac{\rho_B\lambda_e}{u}\,z_o \tag{51}$$

In terms of the three dimensionless groups, and evaluated at z_o, Equation (44) becomes

$$\left(\frac{C}{C_o}\right)_{zo} = \frac{1}{2} + \frac{2}{\pi}\int_o^\infty \exp\left[-\frac{3\lambda_o}{h^2}\psi_1(\lambda)\right] \sin\left[\theta_o\lambda_o\lambda^2 - \frac{3\lambda_o}{h^2}\psi_2(\lambda)\right]\frac{d\lambda}{\lambda} \tag{52}$$

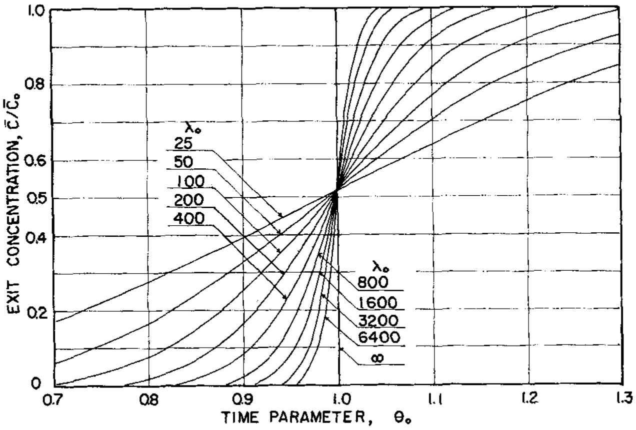

Fig. 4. Effect of reaction group λ_o on breakthrough curve when surface adsorption controls overall rate.

The same type of integral as in Equation (52) is obtained for the solutions for other two-resistance and single-resistance cases. The method of evaluating numerically this form of integral is considered after the solutions to other cases are presented.

EXTERNAL DIFFUSION AND SURFACE ADSORPTION

For this case the intraparticle concentration C is not a function of r. Hence Equation (5) is replaced by

$$\tilde{R} = \rho_B\frac{\delta S}{\delta\theta} \tag{53}$$

and Equation (4) by

$$4\,\pi\,R^2\,k_f\,(\overline{C} - C) = \frac{4}{3}\,\pi\,R^3\,\rho_p\frac{\delta S}{\delta\theta}$$

or

$$\frac{\delta S}{\delta\theta} = \frac{3k_f}{\rho_p R}(\overline{C} - C) \tag{54}$$

and Equation (2) by

$$\frac{\delta C}{\delta r} = 0 \tag{55}$$

Then the problem is described by Equations (1), (3), (53), (54), and (55) with the same initial and boundary equations [Equations (6) and (7)]. Solving Equation (3) for C and substituting in Equation (54) one obtains

$$\bar{C} = \left(\frac{1}{\vec{\lambda}} + \frac{1}{\lambda_f}\right)\frac{\delta S}{\delta\theta} + \frac{1}{\lambda_e} S \tag{56}$$

where

$$\lambda_f = \frac{3k_f}{R\rho_p} \tag{57}$$

The method of solution employed is change variables θ and z to t and x by the use of Equations (8) and (9) and, take the transform with respect to t of the expressions resulting from Equations (56) and (1). The results are:

$$F_t = \left(\frac{1}{\vec{\lambda}} + \frac{1}{\lambda_f}\right) q\, g_t + \frac{1}{\lambda_e} g_t \tag{58}$$

and

$$\frac{d\,F_t}{dx} + \frac{\rho_B}{\epsilon_B} q\, g_t = 0 \tag{59}$$

Equation (58) can be solved for g_t and substituted in Equation (59) giving a first-order ordinary differential equation in F_t. Its solution is

$$F_t = \frac{\bar{C}_o}{p} \exp\left[\frac{-\rho_B\vec{\lambda}}{\epsilon_B}\left(\frac{\lambda_f}{\vec{\lambda} + \lambda_f}\right)\frac{p}{\overleftarrow{\mu}\dfrac{\lambda_f}{\lambda_f + \vec{\lambda}} + p}\right] x \tag{60}$$

The desired result is the inverse transform of F_t. In terms of dimensionless parameters and evaluated at z_o it is

$$\left(\frac{\bar{C}}{\bar{C}_o}\right) = \frac{1}{2} + \frac{2}{\pi}\int_o^\infty \exp\left[-\lambda_o k_o \psi_1(\lambda)\right] \sin\left[\theta_o\lambda_o k_o\lambda^2 - \lambda_o k_o\psi_2(\lambda)\right]\frac{d\lambda}{\lambda} \tag{61}$$

where the reaction and time parameters λ_o and θ_o are the same as before, defined by Equations (49) and (50). Instead of an intraparticle diffusion group the third parameter for this case measures the external diffusion resistance:

External diffusion-surface reaction group

$$k_o = \frac{\lambda_f}{\vec{\lambda} + \lambda_f} \tag{62}$$

For this solution ψ_1 and ψ_2 are the following functions of the integration parameter λ:

$$\psi_1 = \frac{\lambda^4}{1 + \lambda^4} \tag{63}$$

$$\psi_2 = \frac{\lambda^2}{1 + \lambda^4} \tag{64}$$

Equation (61) gives $\bar{C}/\bar{C}_o$ as a function of time for this case in the same form as Equation (52) for surface reaction and intraparticle diffusion.

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General form of solu

	General case (6) External diffusion, intraparticle diffusion, and surface adsorption are rate-determining	Special case 1 (this work) Intraparticle diffusion and surface adsorption are rate-determining	Special case 2 (this work) External diffusion and surface adsorption are rate-determining
Mass balance in sphere	$D_i\left(\frac{\delta^2 C}{\delta r^2} + \frac{2}{r}\frac{\delta C}{\delta r}\right) - \epsilon_p\frac{\delta C}{\delta\theta} - \rho_p\frac{\delta S}{\delta\theta} = 0$	$D_i\left(\frac{\delta^2 C}{\delta r^2} + \frac{2}{r}\frac{\delta C}{\delta r}\right) - \epsilon_p\frac{\delta C}{\delta\theta} - \rho_p\frac{\delta S}{\delta\theta} = 0$	$\frac{\delta C}{\delta r} = 0$
Surface adsorption rate	$\frac{\delta S}{\delta\theta} = \vec{\lambda}C - \overleftarrow{\mu}S = \vec{\lambda}\left(C - \frac{1}{\lambda_e}S\right)$	$\frac{\delta S}{\delta\theta} = \vec{\lambda}C - \overleftarrow{\mu}S = \vec{\lambda}\left(C - \frac{1}{\lambda_e}S\right)$	$\frac{\delta S}{\delta\theta} = \vec{\lambda}C - \overleftarrow{\mu}S = \vec{\lambda}\left(C - \frac{1}{\lambda_e}S\right)$
$\tilde{R}$	$\tilde{R} = 4\pi R^2\bar{n}D_i\left(\frac{\delta C}{\delta r}\right)_{r=R}$	$\tilde{R} = 4\pi R^2\cdot\bar{n}D_i\left(\frac{\delta C}{\delta r}\right)_{r=R}$	$\tilde{R} = \rho_B\frac{\delta S}{\delta\theta} = \left(\frac{3\rho_B}{\rho_p R}\right)\cdot k_f(\bar{C} - C)$
Mass balance in external film	$k_f(\bar{C} - C)_{r=R} = D_i\left(\frac{\delta C}{\delta r}\right)_{r=R}$	$\bar{C} - C = 0$	$k_f(\bar{C} - C) = \frac{1}{3}\rho_p R\cdot\frac{\delta S}{\delta\theta}$
	$\alpha_1 = \left[-\frac{3\lambda_o}{h_2}\cdot\Omega_1\right]; \alpha_2 = \left[\theta_o\lambda_o\lambda^2 - \frac{3\lambda_o}{h_2}\Omega_2\right]$	$\alpha_1 = \left[-\frac{3\lambda_o}{h_2}\Omega_1\right]; \alpha_2 = \left[\theta_o\lambda_o\lambda^2 - \frac{3\lambda_o}{h_2}\cdot\Omega_2\right]$	$\alpha_1 = [-\lambda_o k_o\Omega_1]; \alpha_2 = [\theta_o\lambda_o k_o\lambda^2 - \lambda_o$
	$\Omega_1 = \left[\frac{\psi_1 + k(\psi_1^2 + \psi_2^2)}{(1 + k\psi_1)^2 + (k\psi_2)^2}\right]$	$\Omega_1 = \psi_1$	Same as case 1
	$\Omega_2 = \left[\frac{\psi_2}{(1 + k\psi_1)^2 + (k\psi_2)^2}\right]$	$\Omega_2 = \psi_2$	
Solution	$\psi_1 = \left[\frac{\Phi_1\sin 2\Phi_1 + \Phi_2\sinh 2\Phi_2}{\cosh 2\Phi_2 - \cos 2\Phi_1} - 1\right]$	Same as general case	$\psi_1 = \Phi_1\ (= \Omega_1)$
	$\psi_2 = \left[\frac{\Phi_1\sin 2\Phi_1 - \Phi_1\sinh 2\Phi_2}{\cosh 2\Phi_2 - \cos 2\Phi_1}\right]$		$\psi_2 = \Phi_2\ (= \Omega_2)$
	$\Phi_1 = -h\lambda\left[\frac{1}{2(\lambda^4 + 1)(\sqrt{\lambda^4 + 1} + \lambda^2)}\right]^{1/2}$	Same as general case	$\Phi_1 = \frac{\lambda^4}{1 + \lambda^4}$
	$\Phi_2 = +h\lambda\left[\frac{1}{2(\lambda^4 + 1)(\sqrt{\lambda^4 + 1} - \lambda^2)}\right]^{1/2}$		$\Phi_2 = \frac{\lambda^2}{1 + \lambda^4}$

Dimensionless groups and parameters: h, k, k_o, λ_o, λ_{of}, θ_o, λ_f, and θ_∞ (see notation).

EXTERNAL AND INTRAPARTICLE DIFFUSION

Rosen (9) evaluated the integral solution for the case where external and intraparticle diffusion resistances determined the overall adsorption rate. For these circumstances the relation between C and S is an equilibrium one:

$$S = \lambda_e C \tag{65}$$

rather than Equation (3). This problem is described by Equations (1), (2), (4) (5), (65), (6), and (7). The results are summarized in the fifth column of Table 1. This table also reproduces the results obtained in the preceding sections for the other two-resistance forms of the problem. All the solutions are described in terms of the general form given at the top of the table.

SINGLE-RESISTANCE CASES

As mentioned the solution for $(\bar{C}/\bar{C}_o)_{zo}$ has been obtained previously in other more complicated forms for surface adsorption or external diffusion resistance controlling the rate. However it is desirable to present these solutions in the same form as for the two-resistance cases. This has been done in Table 1, where the result in each case is in terms of the pertinent dimensionless groups. Rosen's solution for intraparticle diffusion controlling the rate is already available (8) in a somewhat similar form. Hence it is not repeated in the table.

It is interesting to note that the form of the solution is exactly the same for surface rate or external diffusion determining the overall rate. As noted in the table for the surface rate case the solution is in terms of the reaction parameter λ_o and θ_o. For the external diffusion case the only change is that λ_{of} is substituted for λ_o. The quantity λ_{of} is the external diffusion dimensionless group defined as

$$\lambda_{of} = \frac{\theta_\infty \lambda_f}{\lambda_e} \tag{66}$$

NUMERICAL EVALUATION OF INTEGRALS

To utilize the solutions in Table 1 it is necessary to evaluate the integrals for a range of values of the dimensionless groups. Rosen (9) developed a method for doing this for the case of intraparticle and external diffusion determining the rate. A somewhat similar numerical method was used in this paper to establish results when intraparticle diffusion and surface adsorption and surface adsorption alone control the overall process.

For the first case Equation (52) was integrated with Weddle's rule (*10*) and by carrying out the numerical work on an IBM-1410 computer. Since the integrand becomes nearly zero as λ increases, the infinite limit of integration can be replaced by the definite limit $j = n(\Delta\lambda)$. The integrand may be written as

$$y_i = e^{-A\psi_1(\lambda_i)} \sin\left[B\,\lambda_i^2 - A\,\psi_2(\lambda_i)\right] \frac{1}{\lambda_i} \tag{67}$$

1

$$\left(\frac{\bar{C}}{\bar{C}_o}\right)_{zo} = \frac{1}{2} + \frac{2}{\pi}\int_o^\infty \left[e^{\alpha_1} \sin \alpha_2\right] \cdot \frac{d\lambda}{\lambda}$$

Special case 3 (9) External diffusion and intraparticle diffusion are rate-determining	Special case 4 External diffusion is rate-determining	Special case 5 Surface adsorption is rate-determining
$D_i\left(\frac{\delta^2 C}{\delta r^2} + \frac{2}{r}\frac{\delta C}{\delta r}\right) - \left(\epsilon_p + \rho_p \lambda_e\right)\frac{\delta S}{\delta \theta} = 0$	$\frac{\delta C}{\delta r} = 0$	$\frac{\delta C}{\delta r} = 0$
$C - \frac{1}{\lambda_e} \cdot S = 0$	$C - \frac{1}{\lambda_e} \cdot S = 0$	$\frac{\delta C}{\delta \theta} = \overrightarrow{\lambda} C - \overleftarrow{\mu} S = \overrightarrow{\lambda}\left(C - \frac{1}{\lambda_e} S\right)$
$\tilde{R} = 4\pi R^2 \cdot \bar{n} \cdot D_i\left(\frac{\delta C}{\delta r}\right)_{r = R}$	$\tilde{R} = 4\pi R^2 \cdot \bar{n} \cdot k_f \cdot \left(\bar{C} - \frac{1}{\lambda_e} S\right)$	$\tilde{R} = \rho_B \cdot \frac{\delta S}{\delta \theta} = \rho_B \overrightarrow{\lambda}\left(C - \frac{1}{\lambda_e} S\right)$
$\bar{C} - C = 0$	$k_f(\bar{C} - C) = \frac{1}{3}\rho_p \cdot R\frac{\delta S}{\delta \theta}$	$\bar{C} - C = 0$
$\alpha_1 = \left[-3\left(\frac{\lambda_o}{h_2}\right)\Omega_1\right]$; $\alpha_2 = \left[2\theta_o\left(\frac{\lambda_o}{h^2}\right)\right]\lambda^2 - 3\left(\frac{\lambda_o}{h_2}\right)\Omega_2\Big]$	$\alpha_1 = [-\lambda_{of}\Omega_1]$; $\alpha_2 = [\theta_o \cdot \lambda_{of}\lambda^2 - \lambda_{of}\Omega_2]$	$\alpha_1 = [-\lambda_o\Omega_1]$; $\alpha_2 = [\theta_o\lambda_o\lambda^2 - \lambda_o \cdot \Omega_2]$
$\Omega_1 = \left[\frac{\psi_1 + k(\psi_1^2 + \psi_2^2)}{(1 + k\psi_1)^2 + (k\psi_2)^2}\right]$ $\Omega_2 = \left[\frac{\psi_2}{(1 + k\psi_1)^2 + (k\psi_2)^2}\right]$	Same as case 2	Same as case 4
Same as general case	Same as case 2	Same as case 4
$\Phi_1 = -\lambda$ $\Phi_2 = +\lambda$	Same as case 2	Same as case 4

where $A = 3\lambda_o/h^2$ and $B = \theta_o\lambda_o$. Then Equation (52) becomes

$$\left(\frac{\bar{C}}{\bar{C}_o}\right)_{z_o} = \frac{1}{2} + \frac{2}{\pi}\int_o^j y(\lambda)\,d\lambda = \frac{1}{2} + \frac{2}{\pi}\frac{3(\Delta\lambda)}{100}\cdot\sum_{i=o}^{n} k_i y_i \tag{68}$$

where $k_i = 1,5,1,6,1,5,2,5,1,6,1,5,2$ . . . . etc.

In the calculations the value of $\Delta\lambda$ was changed as A and B were varied. To ensure reasonable accuracy j was taken large enough to reduce exp $[-A\psi_1(\lambda_i)]/\lambda_i$ to 10^{-5}. Figure 1 illustrates the values of the function y_i for increasing j for the specific case where $\lambda_o = 217$ and $h = 27.9$. It is seen that at $n = 48$, y_i is essentially zero.

Figure 2 shows the results as a plot of $(\bar{C}/\bar{C}_o)_{z_o}$ vs. θ_o for $\lambda_o = 217$. Curves are included for h from 0 to 14.0. Figure 3 illustrates the results for $\lambda_o = 406$. These specific values for the dimensionless groups were chosen because of their relationship to the experimental situation described in the following paper.

For the second case, where surface adsorption is the controlling step, Equation (67) is still applicable, but $A = \lambda_o$, $B = \theta_o\lambda_o$ and the functions $\psi_1(\lambda_i)$ and $\psi_2(\lambda_i)$ are those given in Table 1, special case number 5. The results for this situation are shown in Figure 4, where $(\bar{C}/\bar{C}_o)_{z_o}$ is a function of only two groups θ_o and λ_o. The results given in Figures 2 and 3 for the first case approach those in Figure 4 as the Thiele modulus approaches zero. For example the curve for $h = 0$ in Figure 3 ($\lambda_o = 406$) is essentially the same as the curve in Figure 4 for $\lambda_o = 400$.

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NOTATION

C = intraparticle absorbate concentration, g. mole/cc. of adsorbate-free liquid
$\bar{C}$ = interparticle adsorbate concentration, g. mole/cc. of adsorbate-free fluid. $\bar{C}_o$ is concentration at entrance to bed and $\bar{C}_{z_o}$ at exit
C_1 = constant defined by Equation (29), cm./sec.
C_3 = constant defined by Equation (37)
D_i = effective diffusivity within the particle based upon the spherical area perpendicular to the radial direction, sq.cm./sec.
f_x = Laplace transform of C with respect to x, f_t is transform with respect to t and f_{xt} denotes double transform with respect to x and t
F_x = Laplace transform of $\bar{C}$ with respect to x, F_t is transform with respect to t and F_{xt} denotes double transform with respect to x and t
g = Laplace transform of S
h = intraparticle diffusion dimensionless group (Thiele type of modulus) defined by Equation (36)
i = imaginary quantity, $\sqrt{-1}$
j = $n\,\Delta\,\lambda$
k = D_i/k_fD
k_f = external mass transfer coefficient, cm./sec.
k_o = external diffusion-surface reaction dimensionless group defined by Equation (62)
k_i = coefficient of y_i in Equation (68)
n = average number of spherical particles of radius R in a unit volume of packed bed, cm.$^{-3}$
p = transform parameter with respect to x, sec.$^{-1}$
q = transform parameter with respect to time, sec.$^{-1}$
R = radius of spherical particle, cm.
r = intraparticle radial distance, cm.
$\tilde{R}$ = rate of diffusion of adsorbate across outer surface of spherical particle per unit volume of bed, g. moles/(sec.)(cc.)
S = intraparticle concentration of adsorbate on solid surface, g. mole/(g. of adsorbate-free adsorbent)
t = time variable defined by Equation (9), sec.
u = superficial linear velocity of adsorbate-free fluid, cm./sec.
$W(q)$ = function of q defined by Equation (35)
y_i = integrand in Equation (52) for $\lambda = \lambda_i$, as defined by Equation (66)
x = axial position variable defined by Equation (8), sec.
z = axial distance in bed measured in direction of flow, cm., z_o total bed length

Greek Letters

λ = integration parameter
$\vec{\lambda}$ = adsorption rate constant, cc./(g.)(sec.)
λ_e = adsorption equilibrium constant, $\vec{\lambda}/\vec{\mu}$, cc./g.
λ_f = external diffusion constant, defined by Equation (57)
λ_o = reaction dimensionless group, defined by Equation (49)
λ_{of} = external diffusion dimensionless group, $\theta_x\,\lambda_f/\lambda_e$, defined by Equation (66)
ρ_B, ρ_p = density of packed bed and of particle, respectively, g./cc.
ϵ_B, ϵ_p = void fraction of bed and of particle, respectively, g./cc.
θ = time, sec.
θ_x = holdup time, defined by Equation (51)
θ_o = time dimensionless group, defined by Equation (50)
$\overleftarrow{\mu}$ = desorption rate constant, sec.$^{-1}$
ψ_1, ψ_2 = functions of Φ_1 and Φ_2, defined by Equations (45) and (46) or functions of λ defined by Equations (63) and (64)
Φ_1, Φ_2 = functions of λ, defined by Equations (47) and (48)

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